TABLE II

^{1}H AND ^{11}B NMR CHEMICAL SHIFT VALUES

Compound	B–CH_3[a]	B–C_2H_5[b]	X–CH_3	B–CH_2–X	^{11}B[c]
$CH_3(C_2H_5)BNH_2$[d]	−0.23 s	−0.85 s			−48.4 s
$CH_3(C_2H_5)BN(CH_3)_2$	−0.27 s	−0.86 s	−2.78 s		−45.6 s
$CH_3(C_2H_5)BN_3$	−0.6 s	−0.0 s			−62.8 s
$CH_3(C_2H_5)BOH$[e]	−0.34 s	−0.89 s			−55.3 s
$CH_3(C_2H_5)BOCH_3$	−0.32 s	−0.85 s	−3.60 s		−53.8 s
$CH_3(C_2H_5)BF$	−0.4 d (13 Hz)	−0.95 s			−56.4 d (122 Hz)
$CH_3(C_2H_5)BCl$	−0.95 s	[f]			−30.1 s
$(CH_3)_2BCH_2P(CH_3)_2$[g]	+0.26 d (15 Hz)		−1.04 d (9.4 Hz)	−0.57[h]	+19.0 d (55.4 Hz)
$(CH_3)_2BCH_2As(CH_3)_2$[g]	−0.04 s		−1.08 s	−1.02 s	−6.1 s
$(CH_3)_2BCH_2SCH_3$[g]	+0.08 s		−1.98 s	−1.84 s	+4.0 s
$(CH_3)_2BCH_2Cl$	−0.9 s			−3.4 s	−84.1 s
$(CH_3)_2BCH_2I$	−0.95 s			−2.83 s	−70.6 s

[a] ^{1}H nmr chemical shifts are in ppm without solvent relative to internal tetramethylsilane. [b] At 60 MHz the ethyl protons are equivalent. Peak widths at half-height varied from 4 to 6 Hz. [c] The ^{11}B nmr chemical shifts are in ppm relative to external $BF_3 \cdot O(C_2H_5)_2$. [d] δ(N–H) −3.55 (t, 54 Hz). [e] δ(O–H) −6.56 (s). [f] At 220 MHz the ethyl protons were resolved with the following chemical shifts: $\delta(CH_2\text{–}C)$ −1.34 (q, 7.5 Hz), $\delta(C\text{–}CH_3)$ −1.05 (5, 7.5 Hz). [g] Chloroform solvent. [h] Unresolved coupling.

methylboranes establish the structure of these compounds. The spectra show the expected upfield methyl resonances of area 6 and downfield methylene resonances of area 2. The mass spectra of the $(CH_3)_2BCH_2X$ derivatives show a strong peak at mass 41 corresponding to a $(CH_3)_2B$ fragment which does not occur in the spectra of the methylethylboranes. The high-field boron resonances of $(CH_3)_2BCH_2P(CH_3)_2$, $(CH_3)_2BCH_2As(CH_3)_2$, and $(CH_3)_2BCH_2SCH_3$ suggest that these materials are associated in solution. However, molecular weight determinations (Table III) show that only the phosphorus compound exists as the expected dimer in the vapor phase.

TABLE III

VAPOR DENSITY AND MASS SPECTRAL MOLECULAR WEIGHTS

Compound	Calcd mol wt	Vapor density mol wt[a]	Mass spectral molecular ion
$CH_3(C_2H_5)BN(CH_3)_2$	98.9	99.5	99
$CH_3(C_2H_5)BOCH_3$	85.9	85.9	86
$CH_3(C_2H_5)BF$	73.9	74.5	74
$CH_3(C_2H_5)BCl$	90.4	91.0	90
$(CH_3)_2BCH_2P(CH_3)_2$	232[b]		232
$(CH_3)_2BCH_2As(CH_3)_2$	160	162[c]	160
$(CH_3)_2BCH_2SCH_3$	102	112[c]	102
$(CH_3)_2BCH_2I$	182	180	182

[a] Measured at room temperature. [b] Calculated for dimer. [c] Measured at 125°.

The substitution reactions of α-haloalkylboronic esters occur with rate enhancement to give α-substituted alkylboronic esters as shown by Matteson.[3] In view of these results we believe that although extensive alkyl rearrangement might occur in treatment of I with nucleophiles it would be possible to isolate at least some α-substituted methylboranes as by-products from these reactions. Since high electron density on boron would appear to facilitate the rearrangement, weakly basic nucleophiles were used in all cases. Even though the use of high-vacuum techniques in these experiments allowed investigation of trace products from these reactions, α-substituted methylboranes were observed only in the cases of $(CH_3)_2PH$, $(CH_3)_2AsH$, CH_3SH, and KI. With these nucleophiles the yields of the α-substituted compounds were good and no rearranged products were observed.

In view of the correct structure of the azido compound, the earlier observation that this material decomposes upon pyrolysis to a mixture of borazines is now much more easily understood. Pyrolysis of other *B*-azidoboranes is known to give borazines.[11]

Trimethylamine and trimethylphosphine form adducts with I which were not completely characterized. When equivalent amounts of trimethylamine and I were condensed directly into an nmr tube with chloroform, the proton nmr spectrum showed the presence of trimethylamine adducts of both I and II. The trimethylamine adduct of I, however, could not be isolated due to its facile rearrangement to form the trimethylamine adduct of II (mp 68–70°). Similar experiments with trimethylphosphine resulted only in the isolation of the trimethylphosphine adduct of I (mp 99–100°) which was sublimed at 80° without significant rearrangement.

Acknowledgment.—Support of this work by the National Science Foundation through Grant GP-24266X is gratefully acknowledged. We also express our thanks to Professor Herbert C. Brown for informing us of similar studies prior to publication of his results.[12]

(11) C. Keller, J. Kane, and R. Schaeffer, to be published.

(12) H. C. Brown and Y. Yamamoto, *J. Amer. Chem. Soc.*, **93**, 2796 (1971).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
QUEEN ELIZABETH COLLEGE, LONDON, W.8, ENGLAND

The Preparation of Bis(sulfinylamino) Sulfide (Trisulfur Dinitrogen Dioxide)

BY D. A. ARMITAGE* AND A. W. SINDEN

Received August 24, 1971

The structure determination of trisulfur dinitrogen dioxide[1] showed it to be a sulfinylamino derivative of bivalent sulfur, $S(NSO)_2$. A number of methods of preparation have been reported which involve oxides or halides of sulfur with ammonia, ammonium chloride, or tetrasulfur tetranitride.[2-6] Yields are low and separation of the amino sulfide is often difficult.

(1) J. Weiss, *Z. Naturforsch. B*, **16**, 477 (1961).

(2) M. Becke-Goehring and J. Heinke, *Z. Anorg. Allg. Chem.*, **272**, 297 (1953).

(3) M. Becke-Goehring and J. Heinke, *ibid.*, **298**, 53 (1954).

(4) M. Becke-Goehring, *Progr. Inorg. Chem.*, **1**, 207 (1959).

(5) M. Becke-Goehring and W. L. Jolly, *Inorg. Chem.*, **1**, 77 (1962).

(6) M. Becke-Goehring and G. Magin, *Z. Anorg. Allg. Chem.*, **340**, 126 (1965).

The method reported here utilizes the reaction between sulfur dichloride and *N*-(trimethylsilyl)sulfinylamine and gives a 68% yield of bis(sulfinylamino) sulfide conveniently. The other product, trimethylchlorosilane, was found to be an excellent recrystallization solvent for the amino sulfide. Benzene had been used previously.[5]

$$2Me_3SiNSO + SCl_2 \longrightarrow S(NSO)_2 + 2Me_3SiCl$$

The large, yellow rhombic crystals of the product were sensitive to traces of moisture. They could be conveniently handled in an atmosphere of dry nitrogen. The sample went red on heating and appeared to boil after melting, as previously reported.[2] The infrared spectrum in carbon disulfide contained two major peaks at 1184 and 988 cm^{-1}, attributable to the asymmetric and symmetric stretching vibrations of the sulfinylamino group.[7]

Experimental Section

Sulfur dichloride was purified by distillation in the presence of 10% of phosphorus trichloride,[8] which inhibits disproportionation into sulfur monochloride and chlorine; the distillate was promptly used.

***N*-(Trimethylsilyl)sulfinylamine** was prepared in 88% yield according to the method of Scherer and Horning[9] from tris-(trimethylsilyl)amine[10] and thionyl chloride. The fraction boiling at 108°, $n^{25}\text{D}$ 1.4254, was used.

Bis(sulfinylamino) Sulfide.—In one experiment, 41.4 g (0.307 mol) of the silylsulfinylamine was placed in a 100-ml two-necked flask, fitted with a reflux condenser, and a 50-ml dropping funnel fitted with a by-pass. The whole apparatus was flushed with and maintained under an atmosphere of dry nitrogen, and 14.5 g (0.145 mol) of sulfur dichloride was slowly added to the sulfinylamine, with stirring. The reaction was exothermic, and fine, yellow crystals were deposited. The mixture was heated under reflux for 48 hr to ensure complete reaction. Long, yellow needles formed on cooling and the liquid was then pumped off, trapped (30.2 g), and redistilled to yield trimethylcholorosilane (26.5 g, 87%), bp 57°, $n^{25}\text{D}$ 1.3864.

The yellow crystals were dissolved in 50 ml of hot trimethylchlorosilane, recrystallized, and filtered under a dry nitrogen atmosphere. They were washed with a little cold trimethylchlorosilane and all traces of solvent were pumped off over a period of 3 hr. The crystals melted in sealed tube at 100–101° (lit.[4] mp 100.7°) (14.9 g, 68%). *Anal.* Calcd for $S_3N_2O_2$: S, 61.58; N, 17.93; O, 20.49. Found: S, 61.62; N, 18.11; O, 20.44.

---

(7) G. Kresze, A. Maschke, R. Albrecht, K. Bederke, H. P. Patzschke, H. Smalla, and A. Trede, *Angew. Chem., Int. Ed. Engl.*, **1**, 90 (1962).

(8) B. D. Stone and M. L. Nielson, *J. Amer. Chem. Soc.*, **81**, 3580 (1959).

(9) O. J. Scherer and P. Hornig, *Angew. Chem., Int. Ed. Engl.*, **5**, 729 (1966).

(10) W. L. Lehn, *J. Amer. Chem. Soc.*, **86**, 305 (1964).

CONTRIBUTION FROM THE U. S. BORAX RESEARCH CORPORATION,
ANAHEIM, CALIFORNIA 92801,
AND THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CALIFORNIA,
LOS ANGELES, CALIFORNIA 90024

Boron-11 Nuclear Magnetic Resonance Study of Polyborate Ions in Solution

BY HAMPTON D. SMITH, JR.,*[1] AND RICHARD J. WIERSEMA

Received September 15, 1971

The study of ^{11}B nuclear magnetic resonance is complicated by the fact that boron possesses a nuclear quadrupole moment which causes, in many cases, excessive signal broadening and the resultant overlap of signals which would otherwise appear as distinctly separated resonance lines. Instruments operating at higher magnetic field strengths have slowly become available in recent years and as a result we have seen the unraveling of numerous heretofore unresolved spectra. This is most dramatically illustrated in the areas of boron hydride and carborane chemistry. An extensive review and a very helpful introduction to the nmr of boron compounds is given in a recent book by Eaton and Lipscomb.[2]

The properties of borates, *i.e.*, inorganic boron–oxygen compounds, in aqueous solution have been studied using a variety of techniques.[3] The earliest report of the ^{11}B nmr spectra of borates in solution appears to be that of Shapiro, *et al.*,[4] in which a polyborate ion is postulated to explain a high-field line in aqueous sodium pentaborate.

The existence of polyborates in aqueous solution is inferred from structural studies on crystalline borates. Data obtained from pH titrations, conductance, and cryoscopic studies are best interpreted as involving various polyborate equilibria.[3] The detection of polyborate species by ^{11}B nmr depends on two main factors, the stability of the polyborate ion in solution and the exchange rate of boron atoms between different chemical sites in the molecule. Momii and Nachtrieb[5] studied the borate–polyborate equilibria in aqueous solution using nmr techniques and concluded that three equilibria sufficiently explained the nmr data obtained on sodium pentaborate

$$B(OH)_3 + OH^- \rightleftharpoons B(OH)_4^- \quad K_1 \tag{1}$$

$$2B(OH)_3 + B(OH)_4^- \rightleftharpoons B_3O_3(OH)_4^- + 3H_2O \quad K_3 \tag{2}$$

$$4B(OH)_3 + B(OH)_4^- \rightleftharpoons B_5O_6(OH)_4^- + 6H_2O \quad K_5 \tag{3}$$

Metaborate and tetraborate solutions gave only one nmr signal and provided little information on polyanion formation.

We have undertaken a study of the ^{11}B nmr spectra of aqueous borate solutions at 80 MHz with the hope that more meaningful data can be obtained at the higher magnetic strength.

Results and Discussion

At 80 MHz the ^{11}B nmr spectra of aqueous borate solutions are seen to be considerably more resolved than previously reported. There was, however, no evidence of polyborate formation in metaborate or boric acid solutions. These species presumably represent the extremes in the $B(OH)_4^-$–$B(OH)_3$ system. A plot of the chemical shift *vs.* the $Na_2O:B_2O_3$ ratio (or $B(OH)_4^-$: total boron) for dilute solutions of boric acid (0:1), sodium pentaborate (1:5), sodium tetraborate (1:2), and sodium metaborate (1:1) shows a linear relationship when the single peaks in the nmr spectra of boric acid and sodium metaborate are used as the extremes and the most intense low-field peak in the pentaborate and tetraborate solutions are used. A solution containing Na_2O and B_2O_3 in a 1:3 ratio gave a single

---

(1) To whom correspondence should be addressed at U. S. Borax Research Corp.

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

(3) N. P. Nies and G. W. Campbell, "Boron, Metallo-Boron Compounds and Boranes," Wiley-Interscience, New York, N. Y., 1964, Chapter 3.

(4) T. Onak, H. Landesman, R. E. Williams, and I. Shapiro, *J. Phys. Chem.*, **63**, 1533 (1959).

(5) R. K. Momii and N. H. Nachtreib, *Inorg. Chem.*, **6**, 1189 (1967).