Contribution No. 1141 from the Central Research
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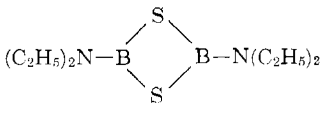
Nemours and Company, Wilmington, Delaware 19898

Boron-Sulfur Ring Compounds

By J. A. Forstner and E. L. Muetterties

Received September 27, 1965

We wish to report a simple, direct synthesis of boron-sulfur ring structures. Hydrogen sulfide attacks trialkylamine boranes at 200° to give hydrogen, alkane, and the cyclic boron sulfides. The type of ring structure obtained is dependent upon the trialkylamine borane employed. With triethylamine borane, the dithiaboretane **1** is formed exclusively, whereas with the methyl analog the six-membered ring **2** (borthiin) is obtained. Compound **2** has been previously described by Wiberg and Sturm.[1] The dithiaboretane structure has been known only with B-sulfhydro[2,3] and B-ethylmercapto substituents.[1] Surprisingly, the highly strained ring of **1** is stable to 200° and does not rearrange to a borthiin structure as does $(HSBS)_2$.[1]



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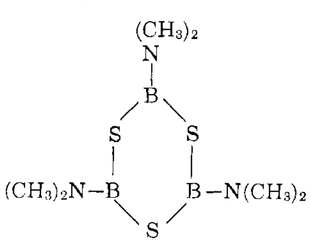

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Experimental Section

Materials.—Hydrogen sulfide (Matheson) was fractionated before use. Triethylamine borane was made in these laboratories and distilled, b.p. 65–68° (2 mm.). Trimethylamine borane (Callery) was used directly.

$(BN(C_2H_5)_2S)_2$.—Triethylamine borane (12.5 g., 0.1 mole) and hydrogen sulfide (6.5 g., 0.2 mole) were heated at 200° for 3 hr. in a 100-ml. stainless steel bomb. The gaseous products were vented and burned in a gas–oxygen flame. The viscous liquid product was heated under vacuum at 100°, yielding a white, solid sublimate. The latter was resublimed and crystallized from pentane to yield 4.2 g. of a white, very hygroscopic solid, soluble in chloroform and carbon tetrachloride, and melting at 70° under vacuum.

Anal. Calcd. for $B_2S_2N_2C_8H_{20}$: C, 41.8; H, 8.78; N, 12.2; B, 9.39; S, 27.9. Found: C, 42.4, 42.1; H, 8.80, 8.98; N (Kjeldahl), 12.0, 12.1; N (Dumas), 12.4, 12.5; B, 9.43, 9.44; S, 28.6, 28.5.

Molecular weight measurements confirm the proposed formulation: calcd. 230; found, cryoscopically in benzene (14 mg./100 g. of benzene), 234; ebullioscopically in carbon tetrachloride (0.11–0.49 mg./100 g. of CCl_4), 232. Mass spectral data, obtained by direct injection into the heated inlet of a spectrometer, confirmed these molecular weight data. The infrared spectrum (as a Nujol mull) included absorptions at 1715 (w), 1695 (w), 1635 (w), 1315 (m), 1265 (s), 1215 (m), 1190 (s), 1130 (s), 1095 (m), 1080 (m), 1065 (m), 995 (m), 980 (m), 945 (m), 885 (m), 830 (m), and 780 (m) cm.$^{-1}$.

The proton n.m.r. spectrum (carbon tetrachloride solution) consists of a distinct methylene quartet and methyl triplet at −3.3 and 1.2 p.p.m., respectively, referenced to external tetramethylsilane. The B^{11} resonance spectrum in the same solvent consists of a singlet at −18.5 p.p.m., referenced to external trimethyl borate.

$(BN(CH_3)_2S)_3$.—Trimethylamine borane (7.3 g., 0.1 mole) and hydrogen sulfide (6.5 g., 0.2 mole) were heated in a 100-ml. stainless steel bomb at 200° for 3 hr. The volatile products were vented and burned. The white, solid product was sublimed twice under vacuum at 200° to yield 4.7 g. of white solid, moderately soluble in acetone and chloroform and melting at 117° (lit.[1] 118°).

Anal. Calcd. for $B_3S_3N_3C_6H_{18}$: C, 27.6; H, 6.91; N, 16.1; B, 12.4; S, 36.9. Found: C, 28.4, 27.6; H, 6.79, 7.12; N, 15.9; B, 12.8; S, 38.6.

The infrared spectrum (as a Nujol mull) consisted of absorptions at 1300 (m), 1230 (w), 1190 (m), 1100 (s), 1080 (m), 1060 (m), 1000 (w), 975 (s), 930 (s), and 715 (w) cm.$^{-1}$.

The molecular weight found ebullioscopically in chloroform (0.20–1.00 mg./100 g. of $CHCl_3$) was 239 (calcd. for trimer, 261). The mass spectrum obtained by direct injection (system held at 70°) demonstrated the molecular weight to be 261. The peak at *m/e* 260 was 70% as intense as that at *m/e* 261, as would be predicted for three boron atoms in the molecule.

The H^1 resonance spectrum ($CDCl_3$ solution) consists of a singlet at −2.4 p.p.m. referenced to external tetramethylsilane. The B^{11} spectrum was a singlet at −20.1 p.p.m., referenced to external trimethyl borate.

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[1] E. Wiberg and W. Sturm, *Z. Naturforsch.*, **8b**, 689 (1953); **10b**, 108 (1955); *Angew. Chem.*, **67**, 483 (1955).

[2] E. Wiberg and W. Sturm, *Z. Naturforsch.*, **8b**, 530 (1953).

[3] A. Stock and O. Poppenberg, *Ber.*, **34**, 399 (1901).

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Phosphorus–Fluorine Chemistry. XVII.[1] Nuclear Magnetic Resonance Studies of Pentafluorophosphates

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Received August 20, 1965

In a previous communication[2] we have reported the unusual rearrangement of the covalent $C_6H_5PF_3N(CH_3)_2$ into the ionic $[C_6H_5PF[N(CH_3)_2]_2]^+[C_6H_5PF_5]^-$. The rearrangement was found to occur most rapidly for the product obtained by the dimethylaminolysis of $C_6H_5PF_4$ in ether at 0°[3]

$$2C_6H_5PF_4 + 2(CH_3)_2NH \longrightarrow C_6H_5PF_3N(CH_3)_2 + [(CH_3)_2NH_2]^+[C_6H_5PF_5]^-$$

We have now carried out the dimethylaminolysis with CH_3PF_4 and find that the $CH_3PF_3N(CH_3)_2$ formed undergoes the same type of rearrangement. While the F^{19} n.m.r. spectrum of $[CH_3PF_5]^-$ shows a simple first-order pattern, the F^{19} spectrum[2,3] of $[C_6H_5PF_5]^-$ is more complicated because of the closeness of the chemical shifts between the two different fluorine atom en-

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[1] Previous paper in this series: R. Schmutzler, *J. Chem. Soc.*, 5630 (1965).

[2] R. Schmutzler, *J. Am. Chem. Soc.*, **86**, 4500 (1964).

[3] R. Schmutzler and G. S. Reddy, *Inorg. Chem.*, **4**, 191 (1965).

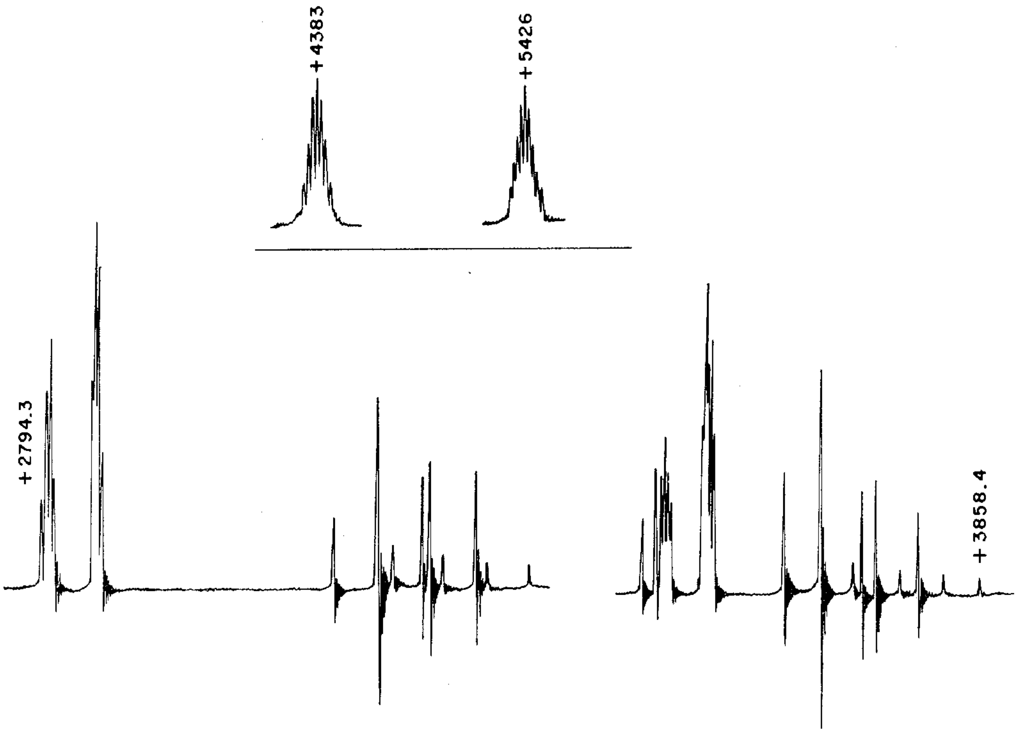

Figure 1.—F^{19} n.m.r. spectrum of $[C_6H_5PF[N(CH_3)_2]_2]^+[C_6H_5PF_5]^-$ in acetonitrile-d_3. The F^{19} spectrum of the cation is shown as an insert.

vironments. An analysis of the F^{19} n.m.r. spectrum of $[C_6H_5PF_5]^-$ was therefore indicated, in order to obtain accurate n.m.r. parameters.

Experimental Section

The salt, $[C_6H_5PF[N(CH_3)_2]_2]^+[C_6H_5PF_5]^-$, was available from previous work.[2]

Reaction of Methyltetrafluorophosphorane with Dimethylamine.—With rigorous exclusion of moisture, 5.0 g. (0.11 mole) of dimethylamine, dried over KOH pellets, was passed into a stirred solution of 12.2 g. (0.1 mole) of methyltetrafluorophosphorane[4] in 30 ml. of ether at 0–5°. The addition being completed in 30 min., the reaction mixture was allowed to warm up to room temperature and was then refluxed for 15 min. After removal of ether by slow distillation through a 5-in. Vigreux column at atmospheric pressure, $CH_3PF_3N(CH_3)_2$ was collected by distillation *in vacuo*, b.p. 48° (140 mm.) (lit.[5] 85°); yield 65%.

Anal. Calcd. for $CH_3PF_3N(CH_3)_2$: C, 24.5; H, 6.2; F, 38.8; N, 9.5; P, 21.0. Found: C, 24.2; H, 6.0; F, 38.7; N, 9.7; P, 21.1.

The residue remaining after the distillation of $CH_3PF_3N(CH_3)_2$ solidified readily. It was sublimed three times *in vacuo* (0.1 mm., bath temperature 90°). The sublimate appeared to deteriorate on repeated sublimation and was found to be extremely deliquescent. Therefore, all manipulations were carried out in a drybox.

Anal. Calcd. for $[(CH_3)_2NH_2][CH_3PF_5]$: C, 19.3; H, 5.9; F, 50.7; P, 16.5. Found: C, 20.9; H, 6.7; F, 50.2; P, 15.4.

In view of the difficulties associated with the handling of this product the analytical data are considered reasonable. Moreover, the identity of the salt is rigorously established from its P^{31} and F^{19} n.m.r. spectra.

N.m.r. Spectra.—All spectra of the pentafluorophosphates were obtained in acetonitrile-d_3 solutions. N.m.r. conditions and instruments were as previously reported.[6] An average of four calibrations were used for each peak in the case of $[C_6H_5PF_5]$-$[C_6H_5PF[N(CH_3)_2]_2]$. Estimated uncertainties in chemical shifts and coupling constants are as follows: δ_P, ± 0.1 p.p.m.; δ_F, ± 0.05 p.p.m.; δ_H, ± 0.01 p.p.m.; J_{P-F}, ± 2 c.p.s.; J_{P-H} and J_{F-H}, ± 0.1 c.p.s.

Results and Discussion

The F^{19} n.m.r. spectrum of freshly prepared C_6H_5-$PF_3N(CH_3)_2$ showed two doublets and two triplets, typical of the trigonal bipyramidal system $R^1R^2PF_3$ with one fluorine atom in equatorial and two in axial positions.[2,3,5,7] However, $C_6H_5PF_3N(CH_3)_2$ was completely absent in the F^{19} spectrum of a sample of the compound stored for a few weeks at room temperature. The original liquid product had solidified and the product was soluble only in polar solvents. A complicated F^{19} spectrum (Figure 1), spread over a wide range, was observed. The peaks between +2794 and +3818 c.p.s. constitute the AB_4 part of an AB_4X system, X being the phosphorus nucleus, and the presence of a species $[RPF_5]^-$ (R = C_6H_5) is indicated. A complete analysis of the F^{19} spectrum of $[C_6H_5PF_r]^-$ was carried out on an IBM 7040 computer, using the program of Ferguson and Marquardt.[8] Initially, the spectrum was treated as two AB_4 systems to obtain trial parameters, and final fit was obtained by analyzing the spectrum as an AB_4X system. Calculated and observed line frequencies are given in Table I. Chemical shifts and coupling constants giving rise to this calculated spectrum are included in Table II. Since calibrations are believed to be accurate only within 0.5 c.p.s., no attempt has been made to obtain agreement better

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[4] R. Schmutzler, *Inorg. Chem.*, **3**, 410 (1964).

[5] R. Schmutzler, *Angew. Chem.*, **76**, 570 (1964); *Angew. Chem. Intern. Ed. Engl.*, **3**, 513 (1964).

[6] G. S. Reddy and R. Schmutzler, *Z. Naturforsch.*, **20b**, 104 (1965).

[7] (a) E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963); (b) E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, *ibid.*, **3**, 1298 (1964).

[8] R. C. Ferguson and D. M. Marquardt, *J. Chem. Phys.*, **41**, 2087 (1964).

TABLE I

CALCULATED AND OBSERVED F^{19} SPECTRUM OF $[C_6H_5PF_5]^-$

Peak No.	Frequency Calculated	Frequency Observed	Intensity Calculated	Intensity Observed[a]
1	2794.3	2794.4	3.24	3.0
2	2797.7	2798.4	5.07	10.0
3	2799.0		5.12	
4	2802.0	2801.8	5.25	10.5
5	2802.1		5.74	
6	2803.5	2803.4	3.59	3.5
7	2834.8	2834.6	4.42	4.2
8	2835.9	2836.2	6.74	13.0
9	2836.5		6.76	
10	2838.1	2838.5	6.89	13.0
11	2839.3		6.93	
12	2840.4	2840.2	4.77	4.5
13	3019.1	3019.2	1.77	2.0
14	3052.7	3053.1	3.93	4.0
15	3065.2	3065.7	1.13	1.0
16	3088.5	3088.5	2.00	2.2
17	3094.3	3094.1	2.83	2.6
18	3104.3	3104.4	0.84	0.8
19	3128.9	3129.1	2.25	2.3
20	3138.1	3138.1	0.69	0.6
21	3169.3	3169.0	0.59	0.5
22	3606.5	3606.4	2.19	2.1
23	3616.0	3616.0	4.09	3.8
24	3621.5	3621.3	4.35	3.8
25	3623.3	3623.5	4.69	4.4
26	3625.4	3625.5	4.81	4.4
27	3627.8	3627.8	3.37	3.1
28	3652.4	3653.0	4.63	4.5
29	3654.5	3654.8	7.19	7.0
30	3655.7	3656.0	7.31	7.2
31	3656.5	3656.8	7.64	7.3
32	3658.2	3658.8	7.91	7.5
33	3661.2	3660.9	5.80	5.3
34	3715.0	3715.2	2.82	2.5
35	3743.6	3743.3	4.92	4.5
36	3769.7	3769.5	0.85	0.8
37	3775.5	3775.6	2.00	2.2
38	3785.7	3786.0	2.41	2.2
39	3804.7	3805.0	0.57	0.6
40	3818.2	3818.0	1.70	1.6
41	3833.8	3834.0	0.44	0.4
42	3858.4	3858.0	0.40	0.4

[a] Observed intensities are accurate to ±10%. More accurate values cannot be obtained due to peak overlaps.

than ±0.5 c.p.s. between calculated and observed spectra. Uncertainties in chemical shifts and coupling constants are therefore believed to be ~0.5 c.p.s.

The F^{19} spectrum of the cation, $[C_6H_5PF[N(CH_3)_2]_2]^+$, is shown as an insert in Figure 1, the fine structure being due to coupling between fluorine and $N(CH_3)_2$ protons.

The novel species, $[C_6H_5PF[N(CH_3)_2]_2]^+$ and $[C_6H_5PF_5]^-$, arise from the rearrangement of $C_6H_5PF_3N(CH_3)_2$, in accordance with

$$2C_6H_5PF_3N(CH_3)_2 \longrightarrow [C_6H_5PF[N(CH_3)_2]_2]^+[C_6H_5PF_5]^-$$

Likewise, F^{19} and P^{31} n.m.r. spectra of freshly distilled $CH_3PF_3N(CH_3)_2$[9] are consistent with trigonal bipyramidal geometry, as in other $R^1R^2PF_3$ compounds.[2,3,5,7] On storage at room temperature for several days the liquid product was found to solidify. The n.m.r. spectra in acetonitrile-d_3 indicate the absence of the original $CH_3PF_3N(CH_3)_2$ and rearrangement according to

$$2CH_3PF_3N(CH_3)_2 \longrightarrow [CH_3PF[N(CH_3)_2]_2]^+[CH_3PF_5]^-$$

has occurred. The doublet–quintet pattern in the F^{19} spectrum is typical of an AB_4X system (X being the phosphorus nucleus). The quartet fine structure of each doublet component is due to coupling between equatorial fluorine and the protons of the CH_3 group in $[CH_3PF_5]^-$, formed in the above rearrangement. A high-field doublet (J_{P-F} = 1032 c.p.s.) is due to the cation, $[CH_3PF[N(CH_3)_2]_2]^+$. The spectra are of nearly first order and coupling constants and chemical shifts were obtained directly without analysis.

F^{19} and P^{31} spectra of the salt $[(CH_3)_2NH_2][CH_3PF_5]$, obtained besides $CH_3PF_3N(CH_3)_2$ in the dimethylaminolysis of CH_3PF_4, are identical with the anion spectra of the rearrangement product, $[CH_3PF[N(CH_3)_2]_2][CH_3PF_5]$. F^{19} and P^{31} n.m.r. parameters for this and the other pentafluorophosphates are given in Table II. Our F^{19} n.m.r. data for $[CH_3PF_5]^-$ are in good agreement with those observed for the same species in solutions of CH_3PF_4 in dimethyl sulfoxide where no salt containing this anion was actually isolated.[10]

TABLE II

N.M.R. PARAMETERS FOR METHYL- AND PHENYL PENTAFLUOROPHOSPHATES

	$[R(\text{or Ar})PF_5]^-$					$[R(\text{or Ar})PF[N(CH_3)_2]_2]^+$			
		δ_F, p.p.m.		J_{P-F}, c.p.s.					
Compound	δ_P, p.p.m.	Axial	Equatorial	Axial	Equatorial	δ_P, p.p.m.	δ_F, p.p.m.	J_{P-F}, c.p.s.	Remarks
$[C_6H_5PF[N(CH_3)_2]_2][C_6H_5PF_5]$	+136.0	+60.9	+57.3	687	820[a]	−56.0	+86.7	1042	. . .
$[CH_3PF[N(CH_3)_2]_2][CH_3PF_5]$	+126.8	+57.5	+46.4	674	831[b]	−70.9	+82.2	1032	*c, d*
$[(CH_3)_2NH_2][CH_3PF_5]$	+124.9	+57.4	+46.8	668	833[b]	. . .	. . .	. . .	*c, d*

[a] $J_{F(\text{axial})-F(\text{equ})}$ = 38 c.p.s. [b] $J_{F(\text{axial})-F(\text{equ})}$ = 35 c.p.s. [c] J_{P-CH_3} in $[CH_3PF_5]^-$ = 21 c.p.s. (from P^{31} n.m.r.). [d] $J_{F(\text{eq})-CH_3}$ in $[CH_3PF_5]^-$ = 8.9 c.p.s. (from F^{19} n.m.r.).

TABLE III

H^1 N.M.R. DATA FOR METHYLPENTAFLUOROPHOSPHATES

Compound	H^1 resonances
$[(CH_3)_2NH_2][CH_3PF_5]$[a]	a. $[(CH_3)_2NH_2]^+$: Broad area, centered at ~7.15 p.p.m.[b] (NH_2) Broad, single peak; δ −2.72 p.p.m.[b] (CH_3N) b. $[CH_3PF_5]^-$: J_{CH_3-P} = 19.8 c.p.s.; $J_{CH_3-F_e}$ = 9.0 c.p.s. δ_{CH_3} −1.05 p.p.m.[b]
$[CH_3PF[N(CH_3)_2]_2][CH_3PF_5]$[a]	a. $[CH_3PF[N(CH_3)_2]_2]^+$: J_{NCH_3-P} = 11.3 c.p.s. J_{NCH_3-F} = ~1.8 c.p.s.; δ_{NCH_3} −2.85 p.p.m.[b] J_{CH_3-P} = 17.0 c.p.s.[c]; δ_{CH_3} −2.17 p.p.m.[b] b. $[CH_3PF_5]^-$: J_{CH_3-P} = 20.0 c.p.s.; $J_{CH_3-F_e}$ = 8.8 c.p.s. δ_{CH_3} −1.01 p.p.m.[b]

[a] Spectra were recorded on solutions in acetonitrile-d_3. [b] An internal tetramethylsilane reference was used. [c] H–F coupling not clearly resolved, estimated 2–3 c.p.s.

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(9) The following n.m.r. parameters were observed for $CH_3PF_3N(CH_3)_2$: $J_{P-F(\text{axial})}$ = 814 c.p.s.; $J_{P-F(\text{equ})}$ = 965 c.p.s.; J_{FF} = 51 c.p.s. $\delta_{F(\text{axial})}$ = +27.6 p.p.m.; $\delta_{F(\text{equ})}$ = +69.5 p.p.m.; δ_P = +37.7 p.p.m. H^1 spectrum: J_{CH_3-P} = 20.2 c.p.s.; $J_{N(CH_3)_2-P}$ = 10.6 c.p.s.; $J_{CH_3-F(\text{axial})}$ = 12.3 c.p.s.; $J_{CH_3-F(\text{equ})}$ = 1.6 c.p.s.; $J_{N(CH_3)_2-F(\text{av})}$ = 2.6 c.p.s. δ_{CH_3} = −1.57 p.p.m.; $\delta_{N(CH_3)_2}$ = −2.78 p.p.m.

(10) E. L. Muetterties and W. Mahler, *Inorg. Chem.*, **4**, 119 (1965).