The relationship of the C^{13}–H coupling constant of chloroform in a chloroform–donor mixture to the basicity of the donor was apparently first noticed by Evans.[24] This relationship is somewhat more complex than the $\Delta\nu$–ΔH one above, because exchange between unassociated and associated chloroform results in a coupling constant which is a weighted average of the constant in pure chloroform and the constant in the base-associated chloroform. Thus, $J(C^{13}\text{–H})$ for chloroform–base mixtures depends not only on ΔH for the hydrogen bond but also on K for the reaction

$$B + HCCl_3 \rightleftarrows B\cdots HCCl_3$$

The $J(C^{13}\text{–H})$ data in Table III for the trimethyl series parallel the $\Delta\nu$ data in suggesting that the silyl derivative is the least basic and the carbon derivative the most basic. The carbon and germanium derivative values have a greater concentration dependence than the silicon compound and this may also be evidence for their greater basicity.

To a first approximation, one might expect basicity to be some function of the effective electronegativity of nitrogen in compounds with very similar steric requirements (for reaction with the reference acid). Comparison of the data in Tables II and III indicates that within a given series the higher the N-methyl C^{13}–H constants, the lower the basicity as measured by $\Delta\nu$. This is obviously a crude generalization, however, as the similar $J(C^{13}\text{–H})$ but differing $\Delta\nu$ values for the trimethylsilyl and -germyl compounds would indicate.

In conclusion, then, the bulk of the data indicates that nitrogen in the silicon derivatives has the highest effective electronegativity and that these compounds are also the least basic. The effective electronegativities vary in the order $M = Si > Ge = C > Sn$ for the trimethyl series and $Si > C > Ge \geqslant Sn$ for the tetrakis series. The chloroform shift data indicate that the basicities toward chloroform as a reference acid vary in the order $C > Ge > Si$ in the trimethyl series and $Ge > Si$ in the tetrakis series.

We believe that these trends can best be rationalized by (p–d)π bonding in the silyl derivatives, a considerably smaller amount in the germanium derivatives (at least in trimethyldimethylaminogermane), and probably none in the tin compounds.

Acknowledgments.—The authors are grateful to Roger Shamel, Richard Griffith, Don Kamens, and Tom Weaver for help in some of the preparations, and are also indebted to Elizabethtown College and the University of Pennsylvania for the use of their nmr spectrometers.

(24) D. F. Evans, *J. Chem. Soc.*, 5575 (1963).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ALBERTA, EDMONTON, ALBERTA, CANADA

The Synthesis and Properties of Difluorodithiophosphoric Acid

BY T. L. CHARLTON AND R. G. CAVELL

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Difluorodithiophosphoric acid, a volatile monomeric compound (bp 72°), has been synthesized by either (1) reaction of iodothiophosphoryl difluoride with hydrogen sulfide or (2) reaction of hydrothiophosphoryl difluoride with sulfur. The acid is slowly hydrolyzed by water and it reacts with chlorine and hydrogen iodide but not with iodine, air, methyl mercaptan, or iodothiophosphoryl difluoride. Amines form salt-like adducts from which the acid is not displaced by hydrogen chloride indicating that the acid is a strong one. Nmr spectra indicate rapid proton exchange in solution. Infrared spectra and mass spectra are reported.

Introduction

Following the recent synthesis of bis(trifluoromethyl)dithiophosphinic acid, $(CF_3)_2PS_2H$, both in our laboratory[1] and by Gosling and Burg,[2] it was of interest to synthesize and study the analogous difluoro acid, difluorodithiophosphoric acid. The salts[3a,b] and the hydrated form[3a] of this acid have only recently been reported. A recent brief communication[3c] mentioned anhydrous difluorodithiophosphoric acid but no preparative details were given. In contrast, the oxygen analog, difluorophosphoric acid,[4] and organic dithiophosphinic acids[5] are well known and have been extensively studied.

Experimental Section

Standard vacuum techniques using a Pyrex-glass apparatus were employed. Stopcocks were lubricated with Apiezon N grease. Infrared spectra were measured with a Beckman IR-12 (4000–300 cm^{-1}) and mass spectra with an AEI MS-9 double-

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(1) R. C. Dobbie, L. F. Doty, and R. G. Cavell, *J. Am. Chem. Soc.*, **90**, 2115 (1968).

(2) K. Gosling and A. B. Burg, *ibid.*, **90**, 2111 (1968).

(3) (a) H. W. Roesky, F. N. Tebbe, and E. L. Muetterties, *ibid.*, **89**, 1272 (1967); (b) M. Lustig and J. K. Ruff, *Inorg. Chem.*, **6**, 2115 (1967); (c) F. N. Tebbe, H. W. Roesky, W. C. Rode, and E. L. Muetterties, *J. Am. Chem. Soc.*, **90**, 3679 (1968).

(4) R. Schmutzler, *Advan. Fluorine Chem.*, **5**, 31 (1965).

(5) L. Maier, *Topics Phosphorus Chem.*, **2**, 43 (1965).

TABLE I

VAPOR PRESSURE OF DIFLUORODITHIOPHOSPHORIC ACID

Temp, °C	−36.8	−36.6[b]	−32.3[b]	−24.8	−20.2[b]	−10.9[b]	−6.6
P(obsd), mm	2.6	2.4	3.3	6.4	9.2	17.7	24.1
P(calcd),[a] mm	2.5	2.6	3.6	6.5	9.2	17.4	22.8
Temp, °C	−3.2[b]	4.4	7.2[b]	13.7	16.4	17.0[b]	22.8
P(obsd), mm	28.2	45.3	52.3	73.3	78.9	86.6	111.4
P(calcd),[a] mm	28.1	44.0	51.4	72.3	83.1	85.6	113.6
Temp, °C	26.0[b]	30.7	35.3[b]	40.9	43.3[b]	49.3	52.3
P(obsd), mm	131.3	159.4	195.1	242.4	267.6	339.2	377.8
P(calcd),[a] mm	131.6	162.0	197.2	247.8	272.0	341.1	380.6

[a] Pressures calculated from eq 3. [b] Pressure measured with temperature descending from the maximum value.

focusing mass spectrometer. Nuclear magnetic resonance spectra were measured with Varian A 56/60 and HA-100 instruments. Fluorine spectra were measured at 56.4 MHz relative to CCl_3F and proton spectra were measured relative to tetramethylsilane.

Materials.—The preparation of hydrothiophosphoryl difluoride and iodothiophosphoryl difluoride have been described previously.[6,7] All chemicals were of Reagent quality and were used without purification. Hydrogen iodide (Matheson) was purified by fractional distillation under vacuum before use.

Preparation of Difluorodithiophosphoric Acid. (a) **From Hydrothiophosphoryl Difluoride and Sulfur.**—In a typical reaction, hydrothiophosphoryl difluoride (0.90 g, 8.83 mmol) was heated to 150° for 48 hr with an excess of sulfur in a 75-cm^3 sealed tube. Fractionation of the volatile products yielded difluorodithiophosphoric acid (0.89 g, 6.67 mmol), collected at −81°, unreacted hydrothiophosphoryl difluoride (0.11 g, 1.11 mmol), collected at −131°, and a mixture of SPF_3, PF_3, and H_2S (total weight 0.08 g), collected at −196°. The over-all yield of SPF_2SH was 76%, or 88% based on hydrothiophosphoryl difluoride consumed.

Higher reaction temperatures and/or longer reaction times led to reduced yields of the acid and increased quantities of SPF_3 and other decomposition products although all of the hydrofluoride was consumed. Lower temperatures and/or short reaction times gave reduced conversion of the hydride to the acid. Traces of $(SPF_2)_2O$[8] were found in some reactions but this product could be readily eliminated by prolonged evacuation of the reaction vessel and the sulfur before introduction of hydrothiophosphoryl difluoride.

(b) **From Iodothiophosphoryl Difluoride and Hydrogen Sulfide.**—In a typical reaction, iodothiophosphoryl difluoride (0.23 g, 0.99 mmol) and hydrogen sulfide (0.04 g, 1.08 mmol) were sealed in a 75-cm^3 reaction tube. Immediately on warming to room temperature, the liquid turned pink and then slowly darkened. After heating at 65° for 7 days, fractionation of the volatile products yielded difluorodithiophosphoric acid, SPF_2SH (0.07 g, 0.50 mmol), collected at −81° and contaminated with a small amount of unreacted iodothiophosphoryl difluoride. The more volatile fractions contained hydrothiophosphoryl difluoride (0.03 g, 0.26 mmol) and H_2S (found mol wt, 35.7) (0.02 g). Molecular iodine remained in the reaction vessel.

Characterization of Difluorodithiophosphoric Acid.—Difluorodithiophosphoric acid is a colorless, volatile liquid. It was characterized by vapor density, molecular weight (calcd for SPF_2SH, 133.9; found, 134.6), and mass spectroscopy, including accurate mass measurement of the parent ion (calcd for $^{32}S_2PF_2H$, *m/e* 133.9225; found, *m/e* 133.9226). The vapor pressure of the acid was measured in an all-glass spiral gauge[9] microtensimeter with both ascending and descending temperatures and with two different samples. The results are given in Table I. The acid is stable at room temperatures and has been stored in sealed vessels for several months without apparent change.

Reactions of Difluorodithiophosphoric Acid. (a) **With Water.**—Difluorodithiophosphoric acid (0.12 g, 0.87 mmol) and a large excess of water were sealed in a 10-cm^3 reaction tube and kept at room temperature for 4 weeks. Fractionation of the volatile products gave only H_2S (0.06 g, 1.67 mmol) and unchanged water. A clear colorless liquid residue remained in the reaction tube. Fluorine nmr of the residues showed only one peak at ϕ 149.5 ppm (relative to $CFCl_3$). No ^1H signal was found.

In another experiment, SPF_2SH (0.13 g, 0.95 mmol), and an equimolar quantity of water (0.02 g, 0.97 mmol) were sealed in a 10-cm^3 reaction tube. After several hours at room temperature, a small amount of a light yellow solid had formed. After 4 days the volatiles were separated yielding unreacted SPF_2SH (0.06 g, 0.44 mmol) and a mixture of SiF_4 and H_2S (0.03 g). A white solid and a colorless liquid remained in the reaction vessel. The residues reacted with acetonitrile and the resultant sample gave neither ^1H nor ^{19}F nmr signals.

(b) **With Dimethylamine.**—Difluorodithiophosphoric acid (0.16 g, 1.17 mmol) and dimethylamine (0.05 g, 1.21 mmol) were sealed in a 10-cm^3 reaction tube. Immediately on warming to room temperature a reaction occurred forming a light yellow solid which melted at a relatively low temperature and resolidified as a crystalline solid. No volatile products were recovered. Nmr spectra of a CH_3CN solution of the solid showed a triplet (τ 7.32, J_{HH} = 5.75 cps) for the ^1H spectrum and a doublet (ϕ 4.63 ppm, J_{PF} = 1151.2 cps) for the ^{19}F spectrum.

(c) **With Methyl Mercaptan.**—An equimolar mixture of SPF_2SH and methyl mercaptan did not react after 8 days at room temperature.

(d) **With Chlorine.**—Difluorodithiophosphoric acid (0.12 g, 0.91 mmol) was combined with molecular chlorine (0.06 g, 0.81 mmol) in a 10-cm^3 reaction tube. After 18 hr at room temperature, separation of the volatiles gave a mixture of HCl, SPF_2Cl,[10a] and PF_2Cl_3[10b] (identified spectroscopically). A light yellow residue (identified as elemental sulfur by its mass spectrum) remained in the reaction tube.

(e) **With Iodine.**—Difluorodithiophosphoric acid was heated to 70° for 10 days with an excess of iodine. Separation of the volatiles yielded unreacted acid plus traces of SPF_3 and HI.

(f) **With Oxygen.**—Difluorodithiophosphoric acid was kept with a large excess of *dry* air in a sealed vessel for 4 days and recovered unchanged.

(g) **With SPF_2I.**—Difluorodithiophosphoric acid (0.11 g, 0.82 mmol) and SPF_2I (0.35 g, 1.54 mmol) were sealed in a 75-cm^3 reaction tube and heated to 75° for 1 month. Fractionation of the volatiles gave a mixture of PF_3 and SPF_3 (0.04 g) and a mixture of SPF_2SH and SPF_2I (0.39 g). The SPF_2SH–SPF_2I

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(6) T. L. Charlton and R. G. Cavell, *Inorg. Chem.*, **6**, 2204 (1967).

(7) T. L. Charlton and R. G. Cavell, *ibid.*, **7**, 2195 (1968).

(8) T. L. Charlton and R. G. Cavell, unpublished work.

(9) R. Cooper and D. R. Stranks, "Techniques of Inorganic Chemistry," Vol. 6, H. B. Jonassen and A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1966, p 1.

(10) (a) J. R. Durig and J. W. Clark, *J. Chem. Phys.*, **46**, 3057 (1967); (b) J. E. Griffiths, R. P. Carter, Jr., and R. R. Holmes, *ibid.*, **41**, 863 (1964).

mixture was resealed in a 75-cm^3 reaction tube and allowed to react at 150° for 10 days. Fractionation of the volatiles gave a further quantity of SPF_3 (0.09 g) and SPF_2SH (0.07 g). Molecular iodine and an orange-brown residue remained.

(h) **With Anhydrous Hydrogen Iodide.**—Equimolar quantities of SPF_2SH and HI did not react when sealed together and left at room temperature overnight. In a second experiment difluorodithiophosphoric acid (0.12 g, 0.91 mmol) was heated with excess hydrogen iodide (0.23 g, 1.76 mmol) for 3 weeks at 160°. Fractionation of the volatile products gave dithiodifluorophosphoric acid (0.04 g, 0.33 mmol) and an inseparable mixture of SPF_2H, SPF_3, PF_3, SiF_4, POF_3, and HI (all identified spectroscopically). Hydrogen sulfide was not present. Molecular iodine and an unidentified yellow-brown solid remained in the reaction tube.

Reactions of the Amine Salt of Difluorodithiophosphoric Acid.—(i) The dimethylamine salt of difluorodithiophosphoric acid prepared as described in part b of the preceding section was sealed with an excess of anhydrous HCl. After 24 hr at room temperatures all of the HCl was recovered unchanged.

(ii) In a similar fashion a sample of the salt was sealed with dry chlorine gas. After 3 days the volatiles contained SPF_2Cl, $SPFCl_2$, $SPCl_3$, SiF_4, and HCl. A yellow residue remained which was not identified.

The Reaction of Hydrothiophosphoryl Difluoride with Hydrogen Sulfide.—Hydrothiophosphoryl difluoride (0.10 g, 0.97 mmol) was heated to 160° with hydrogen sulfide (0.04 g, 1.03 mmol) for 4 days. Separation of the volatile components gave dithiodifluorophosphoric acid (0.01 g, 0.1 mmol), unreacted hydrothiophosphoryl difluoride (0.04 g, 0.35 mmol), and an inseparable mixture of SiF_4, OPF_3, SPF_3, and PF_3 (total weight 0.80 g). A bright yellow residue remained in the reaction tube.

Results and Discussion

Difluorodithiophosphoric acid has been synthesized by two methods: (a) the reaction of sulfur with hydrothiophosphoryl difluoride and (b) the reaction of hydrogen sulfide with iodothiophosphoryl difluoride. Minor yields of the acid are obtained in the reaction of hydrothiophosphoryl difluoride with hydrogen sulfide. The former reaction (a) is the more effective and useful of the two principal methods giving the highest over-all yield of the acid and the purest product. The second reaction (b) is troubled by the difficulty of separating the acid from the iodofluoride and by secondary reactions which reduce the yield of the desired acid. In this case hydrogen iodide produced in the initial step

$$F_2P(S)I + H_2S \longrightarrow F_2P(S)SH + HI \qquad (1)$$

reduces the unreacted iodo compound to the hydride by the fast reaction[7]

$$F_2P(S)I + HI \longrightarrow F_2P(S)H + I_2 \qquad (2)$$

In addition, however, as shown in a separate experiment, the difluoro acid slowly reacts with hydrogen iodide forming hydrothiophosphoryl difluoride, molecular iodine, and a complex mixture of volatile products. Since this reaction is slow at the synthesis temperature of 65° and has an appreciable rate only above 100°, it probably has only secondary importance in the synthesis of difluorodithiophosphoric acid. The combination of reaction 1 with the fast reduction (eq 2) leads to a maximum possible conversion of 50% of the iodothiophosphoryl difluoride to the desired difluorodithiophosphoric acid, and hence this synthetic route is not the most favorable one. A similar situation prevailed in the synthesis of bis(trifluoromethyl)dithiophosphinic acid from the iodide and hydrogen sulfide.[2] In this case fast reduction of the iodo compound by hydrogen iodide[1] occurs with concomitant "anti-Arbuzov" rearrangements[1,11] to the more stable phosphinous state.

Difluorodithiophosphoric acid is a clear, colorless volatile liquid which froze to a glass at low temperatures. The vapor pressure data (given in Table I) are best expressed by the nonlinear equation

$$\log P(\mathrm{mm}) = \frac{-2443.7}{T} - 0.001T + 1.75 \log T + 8.946 \qquad (3)$$

over the range −40 to +50° yielding an extrapolated boiling point of 74°, a heat of vaporization of 6876 cal/mol, and a Trouton constant of 19.8 eu.[12] It behaves as a strong acid readily forming amine salts from which the acid cannot be recovered by treatment with anhydrous hydrogen chloride. Examination of solutions of the amine salts by nmr shows the presence of the $S_2PF_2^-$ anion.[3] Chlorine attacks the salts leading to a variety of phosphorus chlorofluoride products.

The acid does not react with air, oxygen, methyl mercaptan, or iodine. Chlorine reacts with the acid to give a variety of products including HCl, SPF_2Cl, PF_2Cl_3, and residual sulfur. Iodothiophosphoryl difluoride, which reacts with many "active hydrogen" compounds to give SPF_2 derivatives,[7] did not react with difluorodithiophosphoric acid; the majority of the starting material was recovered unchanged along with a small amount of PF_3 and SPF_3. No diphosphorus compounds were obtained.

The complex reaction of difluorodithiophosphoric acid with hydrogen iodide mentioned above is probably best understood by comparison with the analogous reaction of bis(trifluoromethyl)dithiophosphinic acid. The trifluoromethyl acid reacts *quickly* at room temperatures to form the trivalent phosphorus compound, $(CF_3)_2PSH$, iodine, and hydrogen sulfide.[13] The basic process in the reaction probably involves formation of the iodo compound and hydrogen sulfide

$$F_2P(S)SH + HI \longrightarrow F_2P(S)I + H_2S \qquad (4)$$

followed by fast reduction of the iodo compound to hydrothiophosphoryl difluoride (eq 2[7]) giving an over-all conversion of the difluoro acid to hydrothiophosphoryl difluoride and hydrogen sulfide. The reaction products are analogous to those obtained from the reaction of bis(trifluoromethyl)dithiophosphinic acid with hydrogen iodide except for the "anti-Arbuzov" rearrangement which occurs in the trifluoromethyl system. The absence of hydrogen sulfide and the presence of OPF_3, SPF_3, SiF_4, and PF_3 in the products

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(11) J. E. Griffiths and A. B. Burg, *Proc. Chem. Soc.*, 12 (1961).

(12) Nonlinearity of the vapor pressure equation is most pronounced at the lower temperatures. From 10 to 50° the vapor pressure is adequately expressed by the equation $\log P(\mathrm{mm}) = 7.900 - (1732/T)$ which yields a boiling point of 72°, a vaporization enthalpy of 7926 cal/mol, and a Trouton constant of 23 eu, in fair agreement with the results of nonlinear equation.

(13) A. A. Pinkerton and R. G. Cavell, unpublished observations.

Table II

Infrared Spectrum of Difluorodithiophosphoric Acid

Band position, cm⁻¹	Band shape	Intens[a]	Assignment
3660		vw	
2608	PQR	w	SH str
2568		vw	
1820		vw	
1765		vw	
1655		vw	
1450		vw	
1115		vw	
1032	PQR	vw	
936		vs	PF_2 antisym str
891, 886	PQQ'R	s	PF_2 sym str
838	PQR	m	SH bend
811, 807	PQQ'R	w	
739	PQR	w, sh	
732		s	P=S str
722		sh	
524	PQR	m	PS str
389		w	
348	PQR	w	
305		vw	

[a] Abbreviations: m, medium; s, strong; sh, shoulder; v, very; w, weak.

Table III

Mass Spectrum of Difluorodithiophosphoric Acid

m/e	Rel intens[a]	Assignment[b]
136	3.7	$^{34}SPF_2SH$
135	0.8	$^{34}SPF_2S$
134	39.6[c]	PF_2S_2H
133	0.8	PF_2S_2
114	0.8	PFS_2
102	1.4	PF_2SH
101	9.8	PF_2S
95	0.8	PS_2
82	1.7	PFS
69	19.4	PF_2
64	8.7[c]	S_2
63	2.0	PS
50	1.4	PF
34	2.0	H_2S, ^{34}S
33	1.4	HS
32	5.6	S

[a] Intensities are expressed relative to the total ionization, defined as ΣI_n, where n refers to all ions with mass greater than 30 whose intensity is greater than 2% of the base peak. [b] Sulfur-32 isotope assumed unless otherwise indicated. [c] The identity of these peaks was established by mass measurement under high resolution.

is probably best attributed to reaction of hydrogen sulfide with hydrothiophosphoryl difluoride, since a separate experiment indicated that this reaction occurs readily at the temperatures employed and gives the above products. Thermal decomposition of all of the materials and reaction with the glass vessel at the relatively high reaction temperatures may also be responsible for the formation of the observed products.

It is interesting to note that consumption of the trifluoromethyl acid by hydrogen iodide is essentially complete after a few hours at room temperatures[13] whereas the fluoro acid reacts only after prolonged heating. Such a difference in reactivity is surprising in view of the general similarity of the properties of the two acids.

It is also remarkable that reduction of both difluorodithiophosphoric acid and iodothiophosphoryl difluoride[7] leads to the pentavalent hydride, $F_2P(S)H$, whereas both of the trifluoromethyl analogs yield the trivalent isomer $(CF_3)_2PSH$. The difference in reactivity mentioned above and the particular stabilization of the trivalent state by the trifluoromethyl group in contrast to the "normal" pentavalent formulation of secondary thiophosphines[4,11,14] and difluorophosphorus compounds suggest that the CF_3 group exerts a special stabilizing effect on the trivalent phosphorus system which *cannot* be attributed *solely* to the *electronegativity* of the CF_3 group but perhaps is due to the ability of the group to provide extensive electron delocalization through the use of its antibonding (σ^*) orbitals.[15,16]

Difluorodithiophosphoric acid is hydrolyzed by an excess of water to hydrogen sulfide and, presumably, phosphoric acid. With an equimolar quantity of water, the acid was incompletely hydrolyzed; approximately half of the initial quantity of acid was recovered along with SiF_4 and H_2S. The consumed acid therefore reacted with 2 molar equiv of water. The involatile residues were not identified.

In view of the normal gas-phase molecular weight values obtained at low pressures, the gas-phase infrared spectra (given in Table II) are best interpreted in terms of a monomeric species. The band at 2608 cm⁻¹ is obviously best assigned to the S—H stretch and the strong band at 732 cm⁻¹ is probably due to the P=S stretch. The weak band at 524 cm⁻¹ is probably the P—S stretch. Of the four bands between 950 and 800 cm⁻¹, two—those at 936 and 891–886 cm⁻¹—are probably due to antisymmetric and symmetric P—F stretching vibrations and the medium intensity band at 838 cm⁻¹ is probably due to S—H bending since only this band of the four shifts upon deuteration.[17] The rotational structure of the bands, when observed, was either of PQR or PQQ'R type, the latter generally with poorly resolved P and R branches.

Mass spectra (Table III) show expected simple fragmentations but also a substantial proportion of S_2^+ which presumably arises from a rearrangement process, perhaps the process indicated by the metastable peak at *m/e* 30.6 which corresponds to the transition

$$PF_2S_2H^+ \longrightarrow S_2^+ + PF_2H$$

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[14] J. E. Griffiths and A. B. Burg, *J. Am. Chem. Soc.*, **84**, 3442 (1962).

[15] F. A. Cotton and J. A. McCleverty, *J. Organometal. Chem.* (Amsterdam), **4**, 490 (1965); F. A. Cotton and R. M. Wing, *ibid.*, **9**, 511 (1967).

[16] A recent investigation (W. A. G. Graham, *Inorg. Chem.*, **7**, 315 (1968)) suggests that the π-acceptor ability of the CF_3 group is low and may not contribute significantly to the influence of perfluoroalkyl groups. The matter obviously requires further study.

[17] The deuterio acid was prepared by exchanging the hydro acid with DI at room temperatures. The 838-cm⁻¹ band shifts to 740 cm⁻¹ and the S-H stretch at 2608 cm⁻¹ shifts to 1895 cm⁻¹, confirming these assignments.

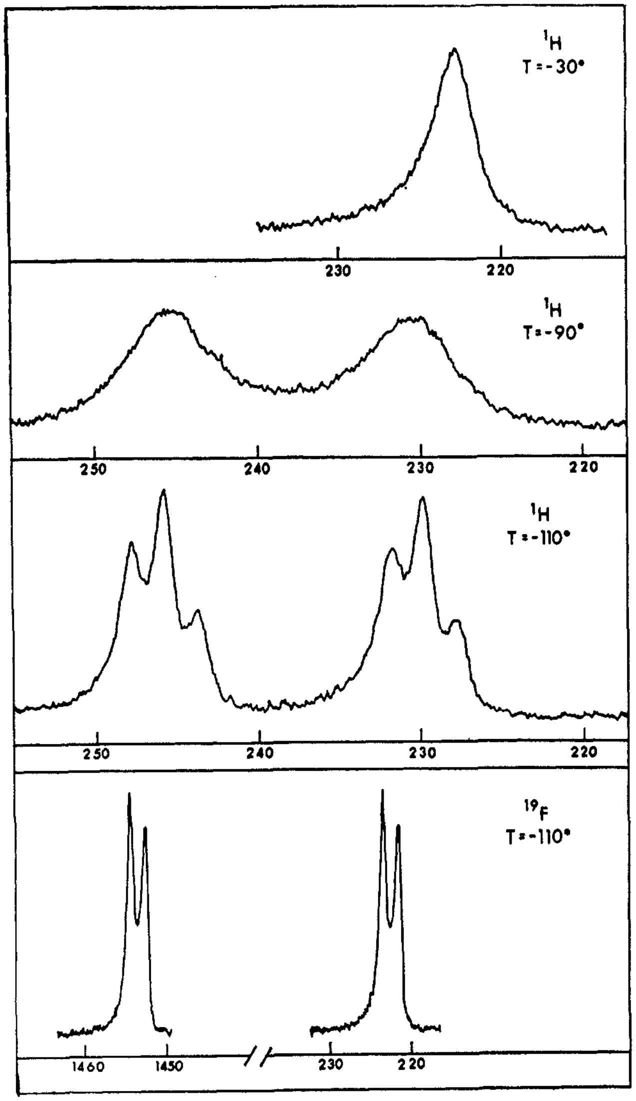

Figure 1.—Low-temperature nuclear magnetic resonance spectra of an approximate 10% solution of difluorodithiophosphoric acid in CCl_3F. The scales give line positions in cycles to *low* field of the standards $(CH_3)_4Si$ for ^1H (measured at 60 Mcps) and CCl_3F for ^{19}F (measured at 56.4 Mcps). Spectra were measured on a Varian A56/60A spectrometer.

(calcd *m/e* 30.6). A metastable peak at *m/e* 97.0 was also observed corresponding to the transition

$$PF_2S_2H^+ \longrightarrow PFS_2^+ + HF$$

(calcd *m/e* 97.0).

The nuclear magnetic resonance spectra of difluorodithiophosphoric acid dissolved in trichlorofluoromethane show a doublet for the ^{19}F resonance spectrum (ϕ 15.75 ppm, J_{PF} = 1211 cps) and a singlet (τ 6.48) for the ^1H spectrum which is consistent with a rapidly exchanging proton.[18] Cooling the sample results in a gradual broadening of the ^1H singlet with resolution into two broad doublets and eventually at $-110°$ (the lowest operating temperature of the spectrometer) the proton spectrum, illustrated in Figure 1, is resolved into a pair of triplets (τ 6.04, J_{PH} = 16.0 cps, J_{FH} = 2.0 cps). At this temperature, as illustrated in Figure 1, the fluorine nmr spectrum shows a doublet of doublets (ϕ 14.85 ppm, J_{PF} = 1231 cps, J_{HF} = 1.9 cps). The spectra are best rationalized in terms of rapid proton exchange at normal temperatures which can be slowed sufficiently by cooling the sample so that normal first-order spin–spin interaction can be resolved. The multiplet pattern is consistent with the localization of the proton on one molecule rather than in a dimer or polymer unit. As yet there is not sufficient data to indicate whether intermolecular proton exchange between two molecules or intramolecular proton exchange between the two sulfur atoms is responsible. We hope to report on a study of the concentration dependence of the spectra of difluorodithiophosphoric acid and bis(trifluoromethyl)dithiophosphinic acid (the spectra of which also can be resolved at low temperatures into spin–spin multiplets[1]) which will distinguish between the inter- and intramolecular proton-exchange mechanism.

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(18) The phosphorus -31 nmr spectrum of a neat sample of the acid at room temperature was a triplet (J_{FP} = 1219 cycles) with a chemical shift of +30.9 ppm relative to P_4O_6.