the chloride ions by N–H···Cl hydrogen bonds. Except for two hydrogen atoms of each methyl group, the atoms of each chain are exactly coplanar.

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The Microwave Spectrum, Structure, and Dipole Moment of Difluorophosphine Oxide[1]

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The microwave spectra of HF_2PO, DF_2PO, and $HF_2P^{18}O$ have been analyzed. The structural parameters are $d(PH) = 1.387 \pm 0.01$ Å, $d(PF) = 1.539 \pm 0.003$ Å, $d(PO) = 1.437 \pm 0.006$ Å, $\angle HPO = 117.9 \pm 2°$, $\angle FPO = 116.3 \pm 1°$, $\angle HPF = 101.9 \pm 1.5°$, and $\angle FPF = 99.8 \pm 0.5°$. The dipole moment was evaluated as 2.65 ± 0.03 D.

Introduction

Difluorophosphine oxide (HF_2PO) was first reported by Treichel, Goodrich, and Pierce[2] as a by-product in the decomposition of HPF_4. This compound and the sulfide analog have now been synthesized and characterized.[3,4] These compounds were the first phosphoryl or thiophosphoryl halides synthesized in which a hydrogen replaced one of the halogens. Their structures are expected to be analogous to the X_3PO series and their chemical and physical properties support this.[3,4] This study was undertaken to determine the detailed structural parameters of HF_2PO and its dipole moment.

Experimental Section

Apparatus.—The spectra were obtained with a conventional Stark modulated spectrometer described previously.[5] The transitions were measured with a precision of about 0.2 Mc. The absorption cell was maintained at about −78° during runs.

Materials.—HF_2PO was prepared by the reaction of F_2POPF_2 with HBr.[4] The DF_2PO was synthesized by substituting DBr enriched to about 75%. $HF_2P^{18}O$ was synthesized by treating PF_2Br with 70% enriched $H_2{}^{18}O$.

Spectrum.—The transitions which were assigned for the three isotopic species are listed in Table I. The rotational constants obtained from the 1_{11}–2_{12}, 1_{01}–2_{11}, and 1_{11}–2_{21} transitions are collected in Table II. The assignment was based on the Stark effect, frequency fit, and expected isotope shifts. Also the near identity of $I_A + I_C - I_B$ (Table II) indicates a plane of symmetry containing hydrogen and oxygen. This is expected for HF_2PO and further supports the assignment.

Stark Effect.—The Stark shift measurements were made with a precision dc power supply[6] (Fluke, Model 413B). The effective guide spacing was determined using the 0 → 1 of OCS ($\mu = 0.7152$).[7] The second-order Stark coefficients measured for HF_2PO are listed in Table III. Several of the assigned low J transitions exhibited Stark effects nonlinear in E^2. This was due to near degeneracies connected by the μ_c component of the dipole moment. One of these was measured and the experimental data are plotted (circles) in Figure 1.

Analysis

Structure.—HF_2PO has six independent structural parameters and the data from three isotopic species should provide seven independent pieces of information. Using conventional methods, described next, we have obtained the structural parameters listed in Table IV. For the convenience of the reader, four bond angles are listed in Table IV although only three are independent. The derived structure is illustrated in Figure 2.

The structural parameters were derived from the coordinates of the atoms. The fluorine "b" coordinate was determined from $I_A + I_C - I_B = 4M_Fb_F^2$. The "$a$" and "$c$" coordinates of the oxygen and the "c" coordinate of the hydrogen were determined from Kraitchman's equations.[8] The "a" coordinate of the hydrogen was too small to be determined this way and was evaluated along with the remaining coordinates from I_A, I_C, and $\Sigma m_ia_i = \Sigma m_ic_i = \Sigma m_ia_ic_i = 0$.

The uncertainties in Table IV were estimated by making additional calculations in which the initial moments of inertia were altered to include their range of experimental uncertainty. The structure can, therefore, be considered a mixed r_s, r_o[9] structure with associated experimental error. The larger uncertainty associated with the hydrogen parameters reflects the difficulty in locating the hydrogen owing to its small "a" coordinate. There is another uncertainty in the parameters arising from vibrational effects which is more difficult to estimate. By analogy with simpler systems it seems reasonable to expect the structural parameters with attached uncertainties to encompass the well-defined average structure.[10]

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TABLE I

TRANSITIONS (Mc) OBSERVED FOR HF_2PO

	HF_2PO		DF_2PO		$HF_2P^{18}O$	
Transition	Obsd	$\Delta\nu^a$	Obsd	$\Delta\nu$	Obsd	$\Delta\nu$
$1_{11} \rightarrow 2_{12}$	21,652.20	0.00	21,355.81	0.01	20,615.46	0.00
$1_{01} \rightarrow 2_{02}$	22,191.80	+0.39	21,830.5[c]	−0.60	21,469.19	+0.09
$1_{10} \rightarrow 2_{11}$	28,198.36	+0.08	27,249.20	+0.18	26,489.61	−0.11
$1_{01} \rightarrow 2_{11}$	32,091.55	+0.02	30,774.57	+0.01	30,542.81	−0.01
$1_{10} \rightarrow 2_{20}$	32,791.48	+0.12	31,417.26	+0.08	31,921.52	+0.02
$1_{11} \rightarrow 2_{21}$	33,331.59	0.00	31,911.43	−0.01	32,775.37	−0.01
$1_{01} \rightarrow 2_{20}$	36,684.96	−0.23	[b]		35,974.92	−0.08
$2_{02} \rightarrow 3_{03}$	31,177.60	+0.49	30,832.55	+1.43	30,086.34	+0.53
$2_{12} \rightarrow 3_{13}$	31,104.41	+0.18	30,767.19	−1.42	29,863.76	+0.52
$2_{21} \rightarrow 3_{22}$			36,438.10	+0.80		
$5_{05} \rightarrow 5_{24}$	32,081.11	+2.56	29,016.07	+0.06		
$5_{15} \rightarrow 5_{14}$	32,081.11	−1.40	29,014.47	−2.12		
$0 \rightarrow 1_{01}$	12,162.71	−0.05				

[a] $\Delta\nu = \nu_{calcd} - \nu_{obsd}$. [b] Not observed owing to interfering lines. [c] Deviation ±1 Mc; all others are ±0.2 Mc.

TABLE II

ROTATIONAL CONSTANTS (Mc) AND MOMENTS OF INERTIA (AMU $Å^2$) FOR HF_2PO[a]

	HF_2PO	DF_2PO	$HF_2P^{18}O$
A	8487.90	8119.96	8472.91
B	7867.89	7551.54	7356.63
C	4594.77	4594.76	4419.61
I_A	59.5590	62.2578	59.6644
I_B	64.2524	66.9441	68.7177
I_C	110.0231	110.0234	114.3836
Δ^b	105.3297	105.3371	105.3303

[a] Estimated accuracy of A, B, and C is ±0.1 Mc. [b] $\Delta = I_A + I_C - I_B$.

TABLE III

STARK COEFFICIENTS ($Mc/V^2/cm^2$) AND DIPOLE MOMENTS (D) FOR HF_2PO

Transition		Obsd	Calcd
$1_{11} \rightarrow 2_{21}$	$M = 0$	$(1.18 \pm 0.02) \times 10^{-5}$	1.17×10^{-5}
$1_{10} \rightarrow 2_{11}$	$M = 0$	$(-4.23 \pm 0.09) \times 10^{-6}$	-4.32×10^{-6}
$0 \rightarrow 1_{01}$	$M = 0$	$(4.81 \pm 0.04) \times 10^{-5}$	4.83×10^{-5}
$1_{01} \rightarrow 2_{02}$	$M = 0$	$(-6.58 \pm 0.13) \times 10^{-6}$	-6.62×10^{-6}
$\mu_a^2 = 3.012$		$\mu_c^2 = 4.026$	$\mu_T^2 = 7.039$
$\lvert\mu_a\rvert = 1.73$		$\lvert\mu_c\rvert = 2.01$	$\lvert\mu_T\rvert = 2.65 \pm 0.03$

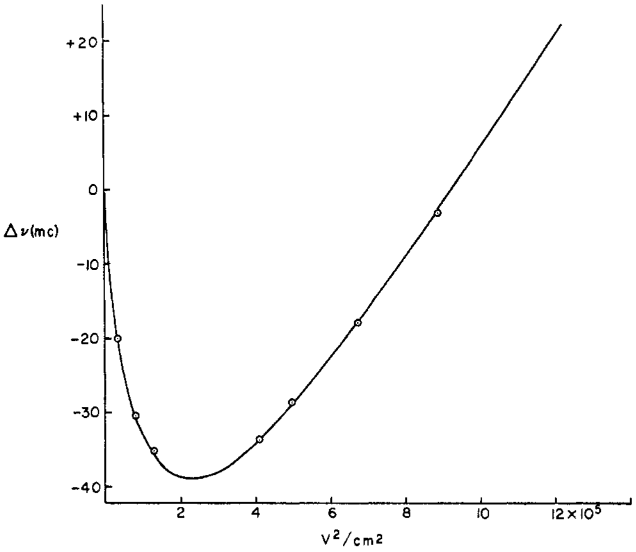

Figure 1.—Experimental and calculated Stark effect for $1_{01} \rightarrow 2_{02}$, $M = 1$. Circles are experimental points.

The structural calculations were checked by computing the nine experimental moments of inertia using the derived structure. Agreement between calculated and experimental moments was about 0.02% or better.

TABLE IV

STRUCTURAL PARAMETERS FOR HF_2PO

$d(PH) = 1.387 \pm 0.01$ Å
$d(PF) = 1.539 \pm 0.003$ Å
$d(PO) = 1.437 \pm 0.006$ Å
$\angle HPO = 117.9 \pm 2°$
$\angle FPO = 116.3 \pm 1°$
$\angle HPF = 101.9 \pm 1.5°$
$\angle FPF = 99.8 \pm 0.5°$

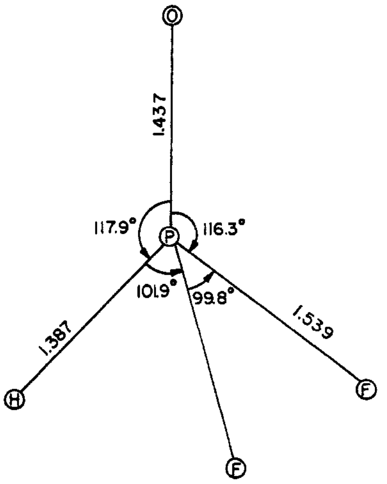

Figure 2.—The structure of HF_2PO.

Dipole Moment.—The components of the dipole moment were determined from the four second-order Stark coefficients listed in Table III. The values obtained were $\lvert\mu_a\rvert = 1.73$ D, $\lvert\mu_c\rvert = 2.01$ D, and $\lvert\mu_T\rvert = 2.65 \pm 0.03$ D. The total dipole moment (μ_T) makes an angle of 40.8° with the c axis. While the orientation of the dipole moment was not determined, the choice based on bond dipole moment calculations (see below) is illustrated in Figure 3.

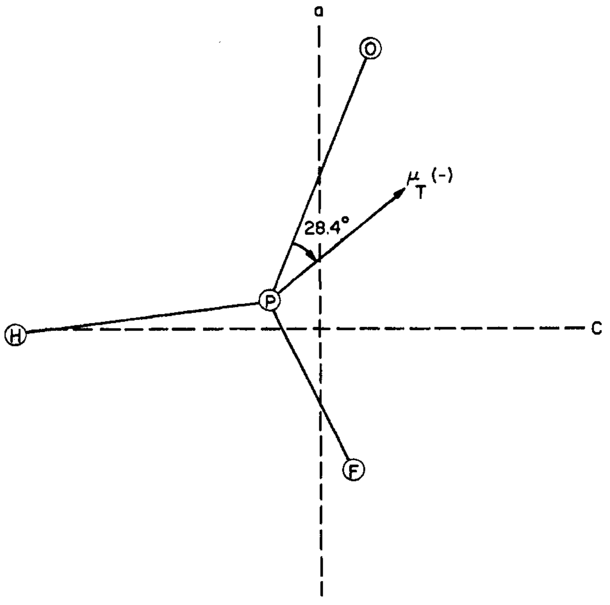

Figure 3.—Projection of HF_2PO on the symmetry plane with likely orientation of the dipole moment.

Although $\kappa = 0.68$ for HF_2PO, many of the degenerate levels in the symmetric top limit are sufficiently close for low J values to give rise to Stark effects which are not second order. These levels are connected by the finite μ_c dipole component. Such Stark effects were observed for the $M = 1$ transitions of $1_{01} \rightarrow 2_{02}$ and $1_{11} \rightarrow 2_{12}$ and the $M = 1$ and $M = 2$ transitions of $2_{02} \rightarrow 3_{03}$ and $2_{12} \rightarrow 3_{13}$. These could be fitted semiquantitatively using the treatment of Golden and Wilson[11] for the case of two interacting levels close and the rest far removed. Also, the $M = 1$ transition of $1_{01} \rightarrow 2_{02}$ was measured quantitatively and checked against calculations. The circles in Figure 1 are the experimental values and the solid curve was calculated using the dipole components reported above. The agreement is within the uncertainties of the experiment.

Discussion

It is interesting to compare the structure of HF_2PO to that determined[5] for HF_2P where $d(\text{PF}) = 1.582 \pm 0.002$ Å, $d(\text{PH}) = 1.412 \pm 0.006$ Å, $\angle\text{FPF} = 99.0 \pm 0.2°$, and $\angle\text{HPF} = 96.3 \pm 0.5°$. Several qualitative structure models can be examined for consistency in rationalizing the differences in the two structures. The most popular theories to consider are those respectively emphasizing (1) electron-pair repulsions,[12] (2) changes in hybridization,[13] (3) d-orbital participation,[14] (4) formal charges, and (5) valence-bond resonance structures. Considering the bond lengths, each of the above models can account for the shorter d(PH) and d(PF) observed in HF_2PO. The first two models also directly include angle variations and can be used to rationalize the increase in the angles observed in HF_2PO. Upon examination of the basis of the various models, the concept of the electronegativity of the atoms attached to phosphorus is fundamental to each. It is this common idea which prevents the HF_2P–HF_2PO system from providing a meaningful distinction between the various models on the basis of the direction of change of their structural parameters.

The large value of the dipole moment for HF_2PO supports a model with a polar PF and even more polar PO bond. This agrees with inferences on the nature of the PO bond from other evidence including reactivity.[15] A prediction of the dipole moment of HF_2PO from bond moments supports the orientation of the dipole moment in Figure 3. Employing bond moments based on PF_3,[16] PH_3,[17] and PF_3O[18] and assuming that F and O are negative and H is positive with respect to phosphorus, the calculated dipole moment is only 0.08 D too small and the orientation is almost exactly that shown in Figure 3. Owing to the obvious differences in electronic structure between the phosphorus compounds with three or four attached atoms, the close agreement is probably fortuitous and does not necessarily imply that the bond dipoles in all four compounds are quite identical. While the value for the PO bond dipole (~2.8 D) seems large on an absolute basis, Phillips, *et al.*,[19] have pointed out that on a comparative basis it is smaller than the NO bond dipole in R_3NO compounds and so does not negate models employing a PO multiple bond.

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Mössbauer Spectra and Electric Dipole Moments of Tin(IV) Compounds Containing the Thiocyanate Group

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Mössbauer and infrared spectra indicate that both $(n\text{-}C_4H_9)_2Sn(NCS)_2$ and $(C_6H_5)_2Sn(NCS)_2$ are bridged polymeric solids with the hydrocarbon groups *trans* to each other. Quadrupole splittings and electric dipole moments reveal a *trans* arrangement of butyl groups in the dipyridyl and *o*-phenanthroline complexes of $(C_4H_9)_2Sn(NCS)_2$ and a *cis* arrangement of phenyl groups in the corresponding complexes of $(C_6H_5)_3Sn(NCS)_2$. This *cis* arrangement is accompanied by large negative isomer shifts relative to a Pd–Sn source at 80°K. Physical measurements suggest a bridged dimer for solid $(C_4H_9)_2Sn(NCS)(C_9H_6NO)$ and 5-coordinated tin in $(C_6H_5)_2Sn(NCS)(C_9H_6NO)$. Dipole moments indicate a *cis* arrangement of hydrocarbon groups for both compounds in benzene solution. Isomer shifts reveal an order of bond polarity Sn–O > Sn–NCS > Sn–Cl.

As a follow-up on Mössbauer and electric moment studies of the effect of complex formation with donor ligands on electron distribution in di-*n*-butyltin dihalides,[3] dibutyl- and diphenyltin diisothiocyanates have been investigated. This study affords a comparison of the relative geometries of the complexes, the relative polarities of the Sn–Cl and Sn–N bonds,

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[2] Abstracted from a portion of the Ph.D. thesis of M. A. M., University of Notre Dame, June 1968.

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