theoretical curves[35] of f's for different values of the overlap integral, $S = \int n\sigma_u dV$. The contribution from the first term in eq 5 is negligible for $b/a > 0.3$. The f's obtained from eq 5 are probably not radically affected for $b/a > 0.3$ even when other configurations are mixed in (3) since only the internuclear distances and not the detailed description of orbitals enter into the second term of eq 5. Agreement between the slopes of theoretical and experimental curves then may be reasonable.

Recent estimates for $(W_1 - W_0)$ and S are around 2.5 eV and 0.3, respectively, for pyridine. This leads to b/a ratios between 0.6 and 0.7 for pyridines. In contradiction to the observed behavior, for $S = 0.3$, f should not vary with ΔH in this region!

The following alternative method seems to give a more acceptable result. The onset of the charge-transfer absorption corresponds to the energy difference between a point P on the potential curves of E where the transition probability vanishes, and the lowest point in the potential curve of N (ignoring the zero-point energy). P need not be the lowest point of the potential curve of E. If E is a repulsive state, $P \geqslant W_1$. Thus the upper limit of the denominator in eq 7 can be equated to the energy of the onset of the transition minus the dissociation energy of N. (If E is an attractive state, this may become the lower limit.) The determination of the energy of onset of CT transition or its variation from complex to complex cannot be done accurately, due to the shape of the bands. It is, however, certainly under 4 eV and probably around 3.5 eV. Due to the lack of alternative methods, the latter value was chosen for a calculation of b/a ratios from eq 7. The experimental f's of the pyridine–iodine series are plotted against the b/a ratios thus obtained in Figure 5.

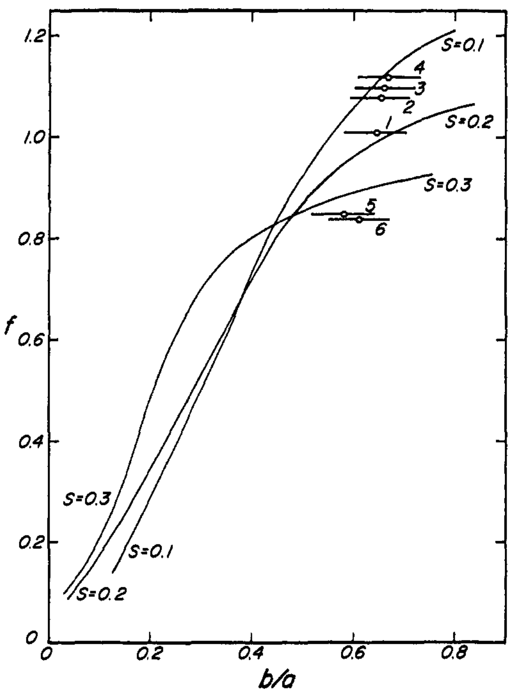

Figure 5. Theoretical curves (eq 5 and ref 33) for oscillator strengths. The points were determined by eq 7. The variation in b/a ratios is due to the use of 1 ± 0.25 eV for the repulsion energy between the donor and acceptor. Donors: (1) pyridine, (2) 2-picoline, (3) 3-picoline, (4) 4-picoline, (5) 2-chloropyridine, (6) 3-chloropyridine.

The curves and experimental points in Figure 5 suggest values around 0.1–0.2 for the overlap integrals in these compounds. These are lower than the value of 0.3 recently suggested for pyridine–iodine complex.[34] In view of the above gross approximations, no definite statement can be made regarding S.

We conclude that these experiments agree with Mulliken's prediction qualitatively and that reliable quantitative treatment of the data is not possible at present.

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(35) From eq 5 with $|r_n - r_\sigma| = 3.7$ Å and $|r_n - r_{n\sigma}| = 1.35$ Å. These values are based on the experimentally observed internuclear distances.[24]

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

Robert L. Kuczkowski

Contribution from the Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48104. *Received October 14, 1967*

Abstract: The microwave spectra of PHF_2 and PDF_2 have been analyzed. Rotational constants are 24551.63, 8895.55, and 6854.02 Mc for PHF_2 and 21898.84, 8635.69, and 6778.49 Mc for PDF_2. The structural parameters of this pyramidal molecule are: $d(PH) = 1.412 \pm 0.006$ Å; $d(PF) = 1.582 \pm 0.002$ Å; $\angle FPF = 99.0 \pm 0.2°$; $\angle HPF = 96.3 \pm 0.5°$. The dipole moment was evaluated as $\mu = 1.32 \pm 0.01$ D.

Difluorophosphine, PHF_2, was recently characterized by Rudolph and Parry.[2] They concluded that its physical and chemical properties were consistent with an expected pyramidal structure. The detailed structural parameters, however, have not been determined and this microwave investigation was undertaken to obtain their values.

Experimental Section

The spectra were measured with conventional 80-kc square-wave Stark modulated spectrometers employing phase-sensitive de-

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(1) This research was supported in part by a grant (GP 6814) from the National Science Foundation, Washington, D. C.

(2) (a) R. W. Rudolph and R. W. Parry, *Inorg. Chem.*, **4**, 1339 (1965); R. W. Rudolph, Ph.D. Thesis, University of Michigan, Ann Arbor, Mich., 1966.

tection[3] at the National Bureau of Standards and the University of Michigan. The NBS spectrometer was described previously.[4] The Michigan spectrometer used a preamplifier, phase-sensitive detector, and square-wave generator purchased from Industrial Components Inc., Beaverton, Ore. Transitions were measured using oscilloscope display swept in both directions. The harmonics of a General Radio frequency multiplier chain locked to a HP Model 100A standard crystal were used. Difference frequencies were measured with a calibrated radio receiver. The frequency standard was monitored with a counter periodically calibrated against radio station WWV. The errors in the frequency measurements (~0.1 Mc) result primarily from the limitation of reproducibly placing frequency markers precisely on the center of an absorption line.

The samples of PHF_2 and enriched PDF_2 were prepared by the method of ref 2a. The spectra were measured at about −78°.

Spectrum

The transitions which were measured and assigned for PHF_2 are listed in Table I. The transitions for PDF_2 are listed in Table II. The assignment was based on the observed Stark effect and the agreement with the calculated spectra. The calculated spectra were obtained with the rotational constants listed in Table III, using computer techniques.[5] Low J transitions were used to obtain the rotational constants to minimize the effect of centrifugal distortion. Pyramidal PHF_2 has a plane of symmetry and the near agreement of $I_c + I_b - I_a$ (see Table III) reflects this and further confirms the assignment.

Table I. Observed and Calculated Spectrum for HPF_2 (Mc/sec)

Transition	Obsd	Calcd
$0 \longrightarrow 1_{11}$	31405.75	31405.65
$0 \longrightarrow 1_{10}$	33447.18	33447.18
$1_{01} \longrightarrow 1_{10}$	17697.61	17697.61
$1_{01} \longrightarrow 1_{11}$	15656.16[a]	15656.08
$1_{11} \longrightarrow 2_{02}$	15656.16[a]	15656.14
$1_{10} \longrightarrow 2_{02}$	13614.17	13614.62
$2_{02} \longrightarrow 2_{12}$	13801.91	13801.46
$2_{12} \longrightarrow 3_{03}$	32708.37	32709.78
$2_{11} \longrightarrow 3_{03}$	26583.90	26585.19
$3_{03} \longrightarrow 3_{12}$	23603.19	23603.15
$4_{04} \longrightarrow 4_{13}$	29059.38	29060.17
$5_{05} \longrightarrow 5_{14}$	36568.92	36572.02
$5_{14} \longrightarrow 5_{24}$	35627.85	35623.80
$5_{23} \longrightarrow 6_{16}$	15154.62	15155.29
$6_{25} \longrightarrow 7_{12}$	28772.95	28777.09
$7_{16} \longrightarrow 7_{26}$	25018.17	25005.48
$7_{34} \longrightarrow 8_{27}$	32716.20	32721.41
$7_{35} \longrightarrow 8_{27}$	34842.98	34851.50

[a] Could not be resolved.

Table II. Observed and Calculated Spectra for DPF_2 (Mc/sec)

Transition	Obsd	Calcd
$0_{00} \longrightarrow 1_{11}$	28677.33	28677.33
$0_{00} \longrightarrow 1_{10}$	30534.74	30534.53
$2_{11} \longrightarrow 3_{03}$	28367.65	28367.80
$2_{12} \longrightarrow 3_{03}$	33939.39	33939.39
$3_{03} \longrightarrow 3_{12}$	20541.00	20540.88
$3_{12} \longrightarrow 3_{22}$	37121.78	37123.31
$3_{21} \longrightarrow 4_{13}$	26952.95	26951.73
$3_{22} \longrightarrow 4_{13}$	27847.95	27848.96
$4_{04} \longrightarrow 4_{13}$	25577.11	25577.48
$4_{13} \longrightarrow 4_{23}$	33666.17	33666.12
$5_{14} \longrightarrow 5_{24}$	29538.87	29536.57
$5_{05} \longrightarrow 5_{14}$	32506.57	32508.73
$5_{24} \longrightarrow 6_{16}$	28652.43	28654.01
$5_{32} \longrightarrow 6_{24}$	29744.38	29746.23
$6_{15} \longrightarrow 6_{25}$	24929.53	24924.22
$6_{24} \longrightarrow 7_{17}$	25762.50	25760.13
$6_{34} \longrightarrow 7_{26}$	33518.06	32519.74
$7_{43} \longrightarrow 8_{35}$	30040.00	30042.13
$7_{44} \longrightarrow 8_{35}$	30132.18	30134.26

Table III. Rotational Constants (Mc/sec) and Moments of Inertia (amu Å²)

	HPF_2	DPF_2
A	24551.63	21898.84
B	8895.55	8635.69
C	6854.02	6778.49
I_a	20.5905	23.0848
I_b	56.8297	58.5397
I_c	73.7569	74.5787
$I_c + I_b - I_a$	109.9961	110.0336

One vibrational satellite of weaker intensity was noted for both species but was not extensively measured. This observation was in accord with the observed infrared spectrum[2a] which indicated a single low-lying vibrational transition at about 358 cm⁻¹.

Structure

The method used to calculate the four structural parameters for pyramidal PHF_2 is a modified Kraitchman substitution calculation similar to one employed for HNF_2.[6] Since the fluorine and phosphorus c coordinates are very small in the principal axis system of the molecule, the modified Kraitchman calculation avoids the necessity of calculating them. The inertial dyadics for PHF_2 and PDF_2 were expressed in the principal axis system of the PF_2 group. From these expressions, the experimentally determined moments of inertia could be related to four new quantities: the principal moments of the PF_2 group, I_a' and I_b', and the coordinates of the hydrogen (or deuterium) in this axis frame, b_H and c_H. The values for these parameters obtained using I_a^H, I_b^H, I_c^H, and I_a^D are listed in Table IV, column I, along with the derived structural parameters. Slightly different values were obtained using I_a^D, I_b^D, I_c^D, and I_a^H, and these are listed in column II. The averages

Table IV. Structural Parameters for PHF_2[a]

	I	II	III
I_a', amu Å²	18.0194	18.0194	
I_b', amu Å²	54.9980	55.0168	
I_c', amu Å²	73.0174	73.0362	
b_H, Å	0.8174	0.7962	
c_H, Å	1.3854	1.3977	
d(PH), Å	1.4081	1.4165	1.412 ± 0.006
d(PF), Å	1.5820	1.5821	1.582 ± 0.002
∠HPF, deg	96.66	96.05	96.3 ± 0.5
∠FPF, deg	99.0	99.0	99.0 ± 0.2

[a] Masses from C. H. Townes and A. L. Shawlow, "Microwave Spectroscopy," McGraw-Hill Book Co., Inc., New York, N. Y., 1955. Column III is considered as having the best values (*cf.* text).

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(4) D. R. Lide, Jr., D. E. Mann, and R. M. Fristrom, *J. Chem. Phys.*, **29**, 444 (1958).

(5) R. Beaudet, Ph.D. Thesis, Harvard University, Cambridge, Mass., 1961.

(6) D. R. Lide, Jr., *J. Chem. Phys.*, **38**, 456 (1963).

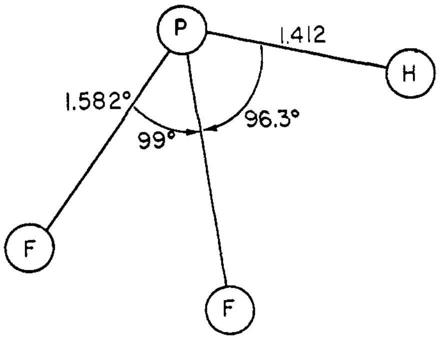

Figure 1. The structure of PHF_2.

of the two structures are listed in column III and are considered the best values of the structural parameters with the present data but ignoring vibrational effects. The structure calculations were checked by computing the six experimentally observed moments.[7] Agreement was better than 0.01%. The uncertainty limits in column III were attached so as to include the two structures in columns I and II plus estimated experimental uncertainties in the rotational constants. For comparison purposes with other structures, it seems reasonable to suggest that the reported structural parameters are within 0.01 Å and 1° of the well-defined average structural parameters.[8] The structure is illustrated in Figure 1.

Dipole Moment

The dipole moment of PHF_2 was determined from Stark effect measurements on the transitions in Table V. The Stark displacement for PHF_2 and OCS (μ = 0.7124 D) at identical electric field settings was measured and from their ratio the Stark coefficients in Table V were evaluated. The dipole moment was calculated as 1.32 ± 0.01 D with $|\mu_b|$ = 1.21 D and $|\mu_c|$ = 0.522 D. This compares with the value of 1.35 ±0.02 D determined previously from dielectric constant measurements.[9]

Table V. Stark Coefficients (Mc/V^2/cm^2) and Dipole Moment for PHF_2

Transition	Obsd	Calcd
$5_{15} \longrightarrow 5_{24}$, $M = 5$	$1.01 \pm 0.02 \times 10^{-6}$	1.01×10^{-6}
$3_{03} \longrightarrow 3_{12}$ $M = 2$	$0.569 \pm 0.005 \times 10^{-5}$	0.569×10^{-5}
$M = 3$	$1.09 \pm 0.01 \times 10^{-5}$	1.08×10^{-5}
	$\lvert\mu_b\rvert = 1.21 \pm 0.01$ D	
	$\lvert\mu_c\rvert = 0.52 \pm 0.01$ D	
	$\lvert\mu_T\rvert = 1.32 \pm 0.01$ D	

While the orientation of the dipole moment was not determined, bond moment arguments, assuming fluorine is negative and hydrogen positive with respect to the phosphorus, indicate that the likely orientation is with the total dipole moment nearly parallel to the bisector of ∠FPF, forming an angle of 27° 03′ with it. This is illustrated in Figure 2.

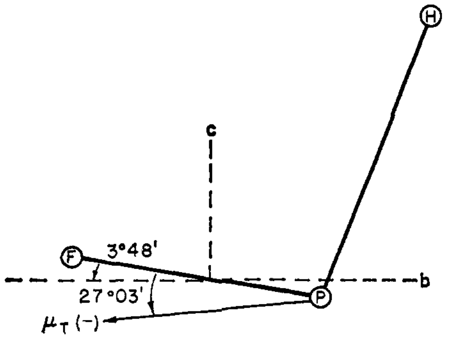

Figure 2. Projection of PHF_2 on symmetry plane with likely orientation of the dipole moment.

Discussion

The structure of HPF_2 closely resembles that of PH_3 and PF_3 except for the PF bond length (see Table VI). There is a marked increase (~0.05 Å) in this parameter for HPF_2 compared with PF_3. A similar increase (~0.03 Å) has been observed in d(NF) in HNF_2 compared with NF_3.[6] This type of increase also is similar to trends observed in halogenated methanes where the carbon–halogen distances decrease as successive hydrogen atoms are replaced by halogens.[10a] The same trend is observed in the fluorinated silanes where the SiF distance is observed to decrease in the series $SiFH_3$ to SiF_4.[10b]

Table VI. Structural Parameters

	HPF_2	PF_3	PH_3
d(PF), Å	1.582 ± 0.002	1.537 ± 0.004[a] 1.535 ± 0.02[c]	
d(PH), Å	1.412 ± 0.006		1.419[b]
∠FPF, deg	99.0 ± 0.2	98.2 ± 0.6[a] 100 ± 2[c]	
∠HPH, deg			93.5[b]
∠HPF, deg	96.3 ± 0.5		

[a] O. L. Hersch, Ph.D. Dissertation, University of Michigan, Ann Arbor, Mich., 1963. [b] C. C. Loomis and M. W. P. Strandberg, *Phys. Rev.*, **81**, 798 (1951). [c] Q. Williams, J. Sheridan, and W. Gordy, *J. Chem. Phys.*, **20**, 164 (1952).

The long PF bond length can reasonably be interpreted as indicating that the electron density in the PF bond is shifted more than usual toward the fluorine atom. This concurs with the interpretation for the large fluorine chemical shift to high field for PHF_2.[11] Morse and Parry[9] also suggested this based on the dipole moment since estimates using bond dipole moments for PH_3 and PF_3 produced values 25% too low for PHF_2.

This structure study does not seem to strongly support an interesting hypothesis that an internal hydrogen bond exists in PHF_2.[12] It was pointed out that this could rationalize the rather low PH stretching frequency and high Lewis basicity of PHF_2. However, the struc-

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(7) R. Schwendeman, *J. Mol. Spectry.*, **6**, 301 (1961).

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(12) R. W. Rudolph and R. W. Parry, *J. Am. Chem. Soc.*, **89**, 1621 (1967).

tural parameters do not suggest a marked attraction between the hydrogen and fluorines, or an increase in d(PH) compared to PH_3, or a decrease in $\angle$FPF compared to PF_3, all of which would be expected consequences of such an interaction. Admittedly, however, it is difficult to completely exclude this interaction.

Acknowledgments. The author thanks Dr. Ralph Rudolph and Mr. Louis Centofanti, who supplied the HPF_2 and DPF_2, and Dr. David Lide, Jr., in whose laboratory the initial measurements were made. The author also thanks Dr. Robert Parry, who suggested the problem to us.

Ring-Segment Exchange Reactions of Cyclic Germthioxanes at Equilibrium

Kurt Moedritzer and John R. Van Wazer

Contribution from the Central Research Department, Monsanto Company, St. Louis, Missouri 63166. *Received September 18, 1967*

Abstract: In mixtures of trimeric dimethylgermanium sulfide and trimeric and/or tetrameric dimethylgermanium oxide, interchange of bridging sulfur with oxygen atoms between the dimethylgermanium groups in the ring structures has been observed by proton nmr. The resulting equilibria between the four trimeric cyclic molecules—the two starting compounds and the two new dimethylcyclogermthioxanes (cyclic mixed oxide–sulfides of dimethylgermanium)—are determined by two equilibrium constants with a third constant relating one of these hexatomic ring structures to the octatomic ring structure of the dimethylgermanium oxide tetramer. Detectable amounts of other cyclic or linear molecules were not present at equilibrium. The reaction paths and the reasons for the observed values of the equilibrium constants are discussed.

Cyclic molecular structures based on germanium atoms alternating with heteroatoms, with the latter being all of one kind, have been known for some time. In the literature, such compounds have been described with the bridging heteroatoms being oxygen,[1,2] sulfur,[1,2] selenium,[3] or nitrogen.[4] However, there have been no reports of the synthesis of such ring compounds where the heteroatoms are of more than one kind. In this paper, by studying the exchange equilibria of bridging oxygen with bridging sulfur in mixtures of trimeric dimethylgermanium sulfide (hexamethylcyclotrigermanium trisulfide) with trimeric/tetrameric dimethylgermanium oxide (hexamethylcyclotrigermoxane and octamethylcyclotetragermoxane), the existence of cyclic molecular species having oxygen as well as sulfur atoms alternating with germanium (*i.e.*, cyclic germthioxanes) has been established. The work discussed herein is related to other investigations from this laboratory dealing with the equilibria in cyclic silthiazanes[5] and cyclic germanosilthianes.[6] Cyclic silthioxanes also have been reported recently.[7]

Experimental Section

Reagents. Trimeric dimethylgermanium sulfide and tetrameric[8] dimethylgermanium oxide were prepared according to the methods reported in the literature.[1,2] The recrystallized substances did not show any proton-containing impurities detectable by proton nuclear magnetic resonance (nmr) and the observed melting points agreed with literature values.[1,2]

Procedures. Seven samples made up of various proportions of trimeric dimethylgermanium sulfide and tetrameric dimethylgermanium oxide in five parts by volume of carbon tetrachloride were sealed in 5-mm o.d. precision nmr tubes. For the equilibrium at 120°, the samples were held at this temperature for various time intervals with the progress of the equilibration reaction checked at that temperature by proton nmr. No change in the spectra upon further heating was observed when the samples had been maintained at this temperature for *ca.* 3 days (high sulfide content) to *ca.* 20 days (high oxide content). To ensure complete equilibration, all samples were kept at 120° for another 24 days, and then analyzed by nmr, with the probe of the Varian A-60 spectrometer being at 120°.

Reequilibration of the 120° samples at room temperature appears to consist of several steps which vary by more than 100-fold in rate. Analyses showed a rapid increase in the amount of tetrameric dimethylgermanium oxide within the first few hours at 25° while reequilibration between the trimeric dimethylgermthioxanes was still underway after several weeks. The reequilibration experiment was terminated after a total of 47 days at room temperature. The nmr probe temperature for these room-temperature spectra was 35°.

The proton nmr spectra were evaluated quantitatively by electronic integration of the peak areas or by cutting out and weighing of Xerox copies of the spectra. The chemical shifts of the resonances observed and their assignments to various segments of the cyclic molecules are presented in Table I. The equilibrium constants were calculated, using the computer programs described previously,[9] by formally treating the "cyclotrigermanium" assemblage as a trifunctional central moiety[5] and the bridging oxygen and sulfur atoms as the exchanging substituents. The mathematical treatment of the equilibria between cyclic trimeric and tetrameric forms of dimethylgermanium oxide has been described elsewhere.[8]

Results and Conclusions

The facile interchange of germanium–oxygen with germanium–sulfur bonds has been demonstrated earlier

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