mainly a delocalized p-electron pair of the chlorine central atom for the formation of a semiionic three-center four-electron p–σ bond pair.[20,35–38] For an ideal semiionic three-center four-electron bond, one should therefore expect f_r to have a value about half that of a covalent ClF bond. The low value of 1.6 mdyn/Å obtained for $ClO_2F_2^-$ obviously fulfills these requirements (covalent ClF bonds show stretching force constants ranging from about 3.5 to 4.7 mdyn/Å) and supports the above bond model.

Acknowledgment.—The authors wish to express their gratitude to Drs. D. Pilipovich and C. J. Schack of Rocketdyne for helpful discussions and to Dr. I. Silvera of the Science Center of North American Rockwell for the use of the Raman spectrophotometer. This work was supported by the Office of Naval Research, Power Branch.

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Microwave Spectrum, Structure, Dipole Moment, and Quadrupole Coupling Constants of Chlorodifluorophosphine[1]

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Received May 11, 1971

The microwave spectra of $PF_2{}^{35}Cl$ and $PF_2{}^{37}Cl$ have been analyzed. The structural parameters are: $d(PF) = 1.571 \pm 0.003$ Å, $d(PCl) = 2.030 \pm 0.006$ Å, $\angle FPF = 97.3 \pm 0.2°$, and $\angle FPCl = 99.2 \pm 0.2°$. The dipole moment was determined to be 0.89 ± 0.01 D and the quadrupole coupling constants in $PF_2{}^{35}Cl$ are $\chi_{aa} = -39.3 \pm 0.3$, $\chi_{bb} = 20.7 \pm 0.3$, and $\chi_{cc} = 18.6 \pm 0.3$ MHz. For $PF_2{}^{37}Cl$, $\chi_{aa} = -31.1 \pm 0.3$, $\chi_{bb} = 16.6 \pm 0.5$, and $\chi_{cc} = 14.5 \pm 0.5$ MHz.

Introduction

Chlorodifluorophosphine, PF_2Cl, and dichlorofluorophosphine, $PFCl_2$, were first prepared more than 30 years ago by the reaction of phosphorus trichloride with antimony trifluoride.[2] At that time the structure of $PFCl_2$ was determined by electron diffraction[3] and compared to previously determined structures[4] of PF_3 and PCl_3. Since that time the structures of PF_3 and PCl_3 have been determined by microwave spectroscopy[5] and also redetermined by electron diffraction.[6,7]

Recently, a more convenient preparation of PF_2Cl was reported.[8] Since this compound was the only member of the series PF_nCl_{3-n} whose structure had not been determined, we decided to undertake a study of the microwave spectrum. Further inducement for such a study was provided by the expectation that a determination of the quadrupole coupling constants would yield information about the bonding in this series of phosphorus compounds, a subject of recent discussion.[9]

Experimental Section

The sample was prepared by reaction of HCl with $(CH_3)_2NPF_2$ by the method recently described.[8] The sample was purified by trap-to-trap distillation.

The spectra were obtained with a 100-kHz Stark-modulated spectrometer employing backward wave oscillators as microwave sources. The sample was contained in a 1.2-m X-band cell cooled by means of Dry Ice. The frequencies of the transitions were measured to an estimated precision of ±0.05 MHz.

Microwave Spectrum

All of the measured rotational transitions appeared as multiplets due to the presence of the quadrupolar chlorine nuclei ($I = {}^3/_2$ for both ^{35}Cl and ^{37}Cl). The spectra of $PF_2{}^{35}Cl$ and $PF_2{}^{37}Cl$ were observed in natural abundance. Assignment of the rotational transitions was based on Stark effects, frequency fit, predicted quadrupole hyperfine splittings, and isotopic shifts. Only *c*-type transitions were observed.

Quadrupole coupling constants in the inertial axis systems were determined for both species by analysis of the hyperfine splittings of transitions with completely resolved multiplets. Hypothetical unperturbed center frequencies were computed for each multiplet and the rotational constants were determined from the hypothetical unsplit frequencies of the 1_{01}–2_{11}, 1_{11}–2_{21}, and 1_{10}–2_{20} transitions. The frequencies of the hyperfine components are compared with calculated frequencies in Table I. The rotational constants, principal moments of inertia, and principal second moments ($P_{aa} = (I_b + I_c - I_a)/2$, etc.) are given in Table II, and the quadrupole coupling constants appear in Table III.

Calculations based on an assumed structure led to the prediction that the *ac* inertial plane would be the

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(1) This work was supported, in part, by grants from the National Science Foundation.

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TABLE I

OBSERVED AND (OBSERVED − CALCULATED[a]) FREQUENCIES[b] OF ROTATIONAL TRANSITIONS IN $PF_2{}^{35}Cl$ AND $PF_2{}^{37}Cl$

		$PF_2{}^{35}Cl$		$PF_2{}^{37}Cl$	
$J \rightarrow J'$	$F \rightarrow F'$	Obsd frequency	$\Delta\nu$[c]	Obsd frequency	$\Delta\nu$
1_{01}–2_{11}	5/2–7/2	18862.55	0.04	18509.90	0.01
	3/2–5/2	18867.09	0.08	18513.52	0.00
	5/2–5/2	...	...	18505.71	0.04
	1/2–1/2	...	...	18506.70	0.07
1_{11}–2_{21}	5/2–7/2	26552.68	0.01	26428.98	−0.01
	3/2–5/2	26557.27	−0.05	26432.65	0.03
	1/2–3/2	26559.61	−0.01	...	...
	3/2–3/2	...	...	26426.98	−0.09
1_{10}–2_{20}	5/2–7/2	25831.42	0.01	25738.67	−0.01
	3/2–5/2	25836.39	−0.01	25742.71	0.03
3_{13}–3_{21}	9/2–9/2	16022.44	−0.04	...	...
	7/2–7/2	16028.87[d]	−0.22	...	...
	5/2–5/2	16026.02	0.02	...	...
	3/2–3/2	16019.42	0.02	...	...
3_{12}–3_{22}	9/2–9/2	10350.19	−0.05	...	...
	7/2–7/2	10357.76	−0.04	...	...
	5/2–5/2	10354.30	0.03	...	...
	3/2–3/2	10346.59	−0.12	...	...
4_{13}–4_{23}	11/2–11/2	8848.73	−0.12	...	...
	9/2–9/2	8853.28	−0.11	...	...
	7/2–7/2	8851.72	−0.08	...	...
	5/2–5/2	8847.24	−0.02	...	...
5_{23}–5_{33}	13/2–13/2	18665.87	−0.25	19397.83	−0.46
	11/2–11/2	18671.23	−0.40	19402.16	−0.49
	9/2–9/2	18669.73	−0.34	19400.92	−0.50
	7/2–7/2	18664.13	−0.44	19396.60	−0.46
5_{24}–5_{32}	13/2–13/2	...	...	22925.28	−0.55
	11/2–11/2	...	...	22928.80	−0.60
	9/2–9/2	...	...	22927.82	−0.57
	7/2–7/2	...	...	22924.30	−0.53
6_{24}–6_{34}	15/2–15/2	16789.01	−0.59	...	...
	13/2–13/2	16793.10	−0.58	...	...
	11/2–11/2	16792.14	−0.58	...	...
	9/2–9/2	16788.10	−0.53	...	...
6_{25}–6_{33}	15/2–15/2	...	...	24267.72	−1.01
	13/2–13/2	...	...	24269.97	−1.03
	11/2–11/2	...	...	24269.43	−1.03
	9/2–9/2	...	...	24267.25	−0.95
7_{25}–7_{35}	17/2–17/2	14488.18	−0.70	...	...
	15/2–15/2	14491.34	−0.65	...	...
	13/2–13/2	14490.84	−0.52	...	...
	11/2–11/2	14487.69	−0.55	...	...
8_{26}–8_{36}	19/2–19/2, 13/2–13/2	11918.08	−0.57	...	...
	17/2–17/2, 15/2–15/2	11920.44	−0.58	...	...
9_{27}–9_{37}	21/2–21/2, 15/2–15/2	9268.56	−0.48	...	...
	19/2–19/2, 17/2–17/2	9270.32	−0.52	...	...
9_{36}–9_{46}	21/2–21/2, 15/2–15/2	...	...	25082.27	−1.89
	19/2–19/2, 17/2–17/2	...	...	25084.52	−1.94
10_{37}–10_{47}	23/2–23/2, 17/2–17/2	...	...	22414.73	−1.90
	21/2–21/2, 19/2–19/2	...	...	22416.62	−1.99
11_{38}–11_{48}	25/2–25/2, 19/2–19/2	17455.83	−1.45	19310.87	−1.77
	23/2–23/2, 21/2–21/2	17457.93	−1.44	19312.58	−1.76
$13_{3,10}$–$13_{4,10}$	29/2–29/2, 23/2–23/2	10631.96	−0.46	...	...
	27/2–27/2, 25/2–25/2	10633.20	−0.58	...	...
$16_{4,12}$–$16_{5,12}$	35/2–35/2, 29/2–29/2	15333.04	−0.60	...	...
	33/2–33/2, 31/2–31/2	15334.43	−0.59	...	...

[a] Calculated using the rotational constants in Table II and the quadrupole coupling constants in Table III. [b] All frequencies are in MHz. [c] $\Delta\nu$ = obsd frequency − calcd frequency; in the case of an unresolved pair of transitions, the calcd frequency is the weighted (proportional to F) mean of the two frequencies. [d] Lower frequency interference.

plane of symmetry (Figure 1). Comparison of the P_{bb} values in Table II for the ^{35}Cl and ^{37}Cl species confirms this prediction.

TABLE II

ROTATIONAL CONSTANTS,[a] MOMENTS OF INERTIA,[b,c] AND PRINCIPAL SECOND MOMENTS[b,d] OF $PF_2{}^{35}Cl$ AND $PF_2{}^{37}Cl$

	$PF_2{}^{35}Cl$	$PF_2{}^{37}Cl$
A	7600.04 ± 0.06 (−0.04)[e]	7597.61 ± 0.06 (−0.02)
B	3754.32 ± 0.06 (−0.01)	3637.55 ± 0.06 (0.01)
C	2908.26 ± 0.12 (0.00)	2838.02 ± 0.12 (0.01)
I_a	66.4965	66.5178
I_b	134.6119	138.9331
I_c	173.7726	178.0734
P_{aa}	120.9440	125.2444
P_{bb}	52.8286	52.8291
P_{cc}	13.6679	13.6887

[a] In MHz. [b] In u Å². [c] Conversion factor used, 505,376 MHz u Å². [d] $P_{aa} = {}^1/_2(I_b + I_c - I_a)$, etc. [e] Numbers in parentheses are differences between observed rotational constants and those calculated from the coordinates in Table IV.

TABLE III

QUADRUPOLE COUPLING CONSTANTS[a] OF $PF_2{}^{35}Cl$ AND $PF_2{}^{37}Cl$

	$PF_2{}^{35}Cl$	$PF_2{}^{37}Cl$
χ_{aa}	−39.3 ± 0.3	−31.1 ± 0.3
χ_{bb}	20.7 ± 0.3	16.6 ± 0.5
χ_{cc}	18.6 ± 0.3	14.5 ± 0.5
χ_{zz}[b]	−46.6	−36.7
χ_{yy}	20.7	16.6
χ_{xx}	25.9	20.1
θ_{az}[b]	18.5°	18.3°

[a] In MHz. [b] The angle between the a and z axes, θ_{az}, was determined from the structure (Table IV). The b and y axes are parallel.

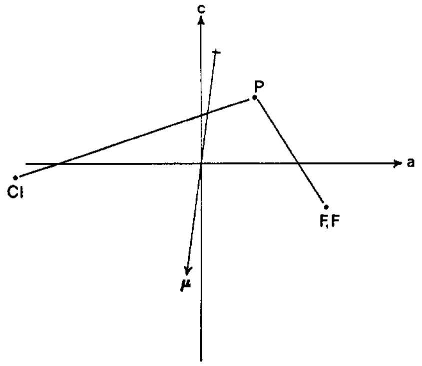

Figure 1.—Projection of PF_2Cl in its plane of symmetry.

Quadrupole Coupling Constants

The quadrupole coupling constants in Table III are referred to inertial axes. If the b axis is perpendicular to the plane of symmetry, the quadrupole coupling constants in Table III are related to the principal quadrupole coupling constants, χ_{xx}, χ_{yy}, χ_{zz}, by a single parameter which may be taken to be the angle between the a and z axes, θ_{az}. If the y axis is taken to be parallel to the b axis, the relations are

$$\chi_{aa} = \chi_{zz} \cos^2 \theta_{az} + \chi_{xx} \sin^2 \theta_{az}$$

$$\chi_{bb} = \chi_{yy}$$

$$\chi_{cc} = \chi_{zz} \sin^2 \theta_{az} + \chi_{xx} \cos^2 \theta_{az}$$

If the PCl bond line is assumed to be the z principal axis of the quadrupole coupling constant tensor, the angle θ_{az} may be determined from the structure and χ_{xx} and χ_{zz} may be calculated. The values of θ_{az} for $PF_2{}^{35}Cl$ and $PF_2{}^{37}Cl$ and the resulting values of χ_{xx} and χ_{zz} are shown in Table III.

Deviation of the charge distribution near the chlorine nucleus from cylindrical symmetry about the

z axis is measured by $\Delta = \chi_{xx} - \chi_{yy}$. If the PCl bond were a pure σ bond and if the small effects of the adjacent atoms could be neglected, Δ would be zero. Asymmetry of the charge distribution about the PCl bond in PF_2Cl presumably arises from the interaction of the chlorine p_x and p_y orbitals with suitable phosphorus orbitals with resultant loss of electrons from the p_x and p_y orbitals. If π_x and π_y are the numbers of electrons lost from the p_x and p_y orbitals due to this bonding interaction, it may be shown that[10]

$$\Delta/eQq_{\text{at}} = 3(\pi_x - \pi_y)/2$$

where $eQq_{\text{at}} = -109.74$ MHz for ^{35}Cl.[11] For $PF_2{}^{35}Cl$, $\Delta = 5.2$ MHz (Table III) and consequently $\pi_x - \pi_y = -0.03$; *i.e.*, 0.03 more electron is lost from the p_y orbital (perpendicular to the plane of symmetry) than from the p_x orbital. The minimum π-bond character of the PCl bond consistent with these numbers is 1.5%, which would occur if $\pi_x = 0$ and $\pi_y = 0.03$.

The quadrupole coupling constants may also be used to estimate the ionic character of the PCl bond. For this purpose we use the relation[12]

$$\chi_{zz}/eQq_{\text{at}} = [1 - I - s^2 + d^2 - (\pi_x + \pi_y)/2]$$

in which I is the ionic character. In this equation s^2 and d^2 are the s and d character of the chlorine atomic orbital involved in the PCl bond. Assuming $s^2 - d^2 = 0.15$[13] and $(\pi_x + \pi_y)/2 = 0.015$, the ionic character of the PCl bond is found to be 41%.

The quadrupole coupling constant of ^{35}Cl in solid PF_2Cl has been determined by analysis of the nuclear quadrupole resonance spectrum. The value obtained was 44.8 MHz.[14] Dailey[13] found that for a series of chlorohydrocarbons the average ratio of the gas-phase quadrupole coupling constant to the value in the solid state is 1.083. By using the gas-phase value from the microwave spectrum (46.6 MHz) and the solid-state value, the ratio for PF_2Cl is found to be 1.040.

Stark Effect and Dipole Moment

The dipole moment of PF_2Cl was determined from the Stark shifts in frequency of three $J = 1 \rightarrow 2$ transitions. The Stark shifts were measured using a square-wave generator which has provision for dc voltage offset of the base of the square wave. The electric fields in the sample cell were calibrated by measuring the Stark shifts of the $J = 0 \rightarrow 1$ and the $J = 1 \rightarrow 2$ transitions of OCS ($\mu = 0.7152$ D).[15]

The chlorine nuclear quadrupole coupling complicates the calculation of Stark shifts[16] and consequently the usual method of comparison of slopes of plots of $\Delta\nu$ *vs.* E^2 (E = electric field) with theoretical calculations was abandoned. Instead, the frequencies of various Stark components were measured at different values of the electric field and the individual shifts in frequency from the appropriate hypothetical unsplit frequency were compared with theoretical calculations. The values of $\mu_a{}^2$ and $\mu_c{}^2$ ($\mu_b{}^2 = 0$ by symmetry) were varied until the best fit (in the least-squares sense) was obtained between theoretical and experimental Stark shifts. In order to simplify the Stark patterns, only fairly high Stark fields were employed. This had the disadvantage of reducing the resolution, so that in most cases the measured frequencies were average frequencies of two unresolved components. As a result, the differences between observed and calculated Stark shifts were somewhat larger than is typical for microwave Stark effect measurements. (The mean deviation was 0.36 MHz.) Also, the high fields led to rather large Stark shifts: the smallest measured shift was 5.12 MHz, the largest was 69.92 MHz, and the mean measured shift for 29 Stark components was 23.09 MHz. Recent Stark calculations in our laboratory suggest that for shifts of this magnitude nonnegligible deviations from second-order perturbation theory must be expected.

To calculate the Stark shifts a computer program was written to determine the approximate eigenvalues of the Hamiltonian

$$H = H_{\text{R}} + H_{\text{Q}} + H_{\text{S}}$$

Here, H_{R} is the rigid rotator Hamiltonian, H_{Q} is the contribution from quadrupole coupling, and H_{S} is the contribution from the Stark effect. The program requires as input the rotational constants, the quadrupole coupling constants, and the components of the dipole moment. The rotational constants and quadrupole coupling constants are taken from the analysis of the zero-field spectrum. The approximations in the program are such that if the quadrupole coupling constants are zero, the correct second-order Stark shifts are obtained, whereas if the dipole-moment components are all zero, the correct first-order hyperfine splittings are obtained.

A second computer program was written to compute the relative intensities of the Stark components. The intensities were used to aid in the assignment. It was found that for the fields employed neither the low field nor the high field patterns of Stark lobes were of much help in the assignment.

A third computer program numerically computes derivatives of the Stark shifts with respect to variations in $\mu_a{}^2$ and $\mu_c{}^2$, computes frequencies and derivatives of frequencies for the desired transitions, averages the frequencies and derivatives for the unresolved components, and varies $\mu_a{}^2$ and $\mu_c{}^2$ to give the best least-squares fit to the observed shifts in frequencies.

The dipole moment components obtained by means of the analysis just described are $\mu_a = 0.103 \pm 0.010$ D and $\mu_c = 0.884 \pm 0.010$ D. The total dipole moment is $\mu = 0.890 \pm 0.010$ D. Although the orientation of the dipole moment is not uniquely determined, consideration of the relative electronegativities of F and Cl suggests the orientation shown in Figure 1.

The dipole moment of PF_2Cl was previously determined by Morse[17] by the heterodyne beat method. The value obtained ($\mu = 0.931 \pm 0.012$ D) is somewhat higher than that derived from our Stark effect measurements.

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Molecular Structure

There are four structural parameters in PF_2Cl. These may be taken to be the PF and PCl bond distances and the FPF and FPCl angles. Since five independent moments of inertia have been obtained, a complete determination of the structure is possible.

The fluorine b coordinates can be determined from the relation $P_{bb} = 2m_F b_F^2$ using the P_{bb} value for either species. The near-equality of the P_{bb} values shown in Table II leads to essentially identical b_F values. The a and c coordinates of the chlorine atom were first found using Kraitchman's equations:[18] $|a_{Cl}| = 1.4814$ Å and $|c_{Cl}| = 0.1052$ Å. It is known that a Kraitchman coordinate as small as 0.1 Å is likely to be underestimated.[19] Consequently, the chlorine c coordinate was included with the a and c coordinates of the phosphorus and fluorine atoms and these five coordinates were determined from I_a and I_c of $PF_2{}^{35}Cl$ and from the first and second moment conditions, $\Sigma m_i a_i = \Sigma m_i c_i = \Sigma m_i a_i c_i = 0$. As a result of this calculation, $|c_{Cl}| = 0.1067$ Å. The very small difference in the chlorine c coordinate by the two procedures indicates that the vibrational effects in the rotational spectrum and on the determination of the structure are probably small.

The final values of the coordinates and the bond distances and bond angles are given in Table IV. These structural parameters are r_0 parameters, and the uncertainties in them include an estimate of the vibrational effects on the nuclear coordinates.

TABLE IV
PRINCIPAL AXIS COORDINATES[a] AND BOND DISTANCES AND BOND ANGLES FOR PF_2Cl

	a	b	c
P	0.4438	0	0.5362
Cl	−1.4813	0	−0.1067
F	1.0015	±1.1791	−0.3389

PF, Å	1.571 ± 0.003	∠FPF, deg	97.3 ± 0.2
PCl, Å	2.030 ± 0.006	∠FPC, deg	99.2 ± 0.3

[a] In Å. For these coordinates $\Sigma m_i a_i = \Sigma m_i c_i = \Sigma m_i a_i c_i = 0.0000$. The structural parameters given here are r_0 parameters.

Discussion

The structural parameters of the compounds in the series PF_nCl_{3-n} are compared in Table V. The structural parameters of PF_2Cl are similar to those of the other chlorofluorophosphines and intermediate between the values for PCl_3 and PF_3. In fact, only the parameters of $PFCl_2$ depart from a smooth trend and this is probably due to the large uncertainty inherent in older electron diffraction work.

TABLE V
STRUCTURAL PARAMETERS FOR THE CHLOROPHOSPHINES[a]

	PF, Å	PCl, Å	Angle, deg ∠FPF	 ∠FPCl	 ∠ClPCl	Ref
PF_3	1.569		97.7			6, ED
	1.563		96.9			5a, MW
PF_2Cl	1.571	2.030	97.3	99.2		This work
$PFCl_2$	1.55	2.02		102	102	3, ED
PCl_3		2.039			100.5	7, ED
		2.043			100.1	5b, MW

[a] Caution is required when making comparisons of the data in this table. The electron diffraction values are r_a parameters, whereas the microwave entries are r_0 values except for PF_3, for which equilibrium values are shown. Except for $PFCl_2$, which is from an older electron diffraction study, differences greater than 0.01 Å and 0.5° are probably significant. (See K. Kuchitsu and S. Konaka, *J. Chem. Phys.*, **45**, 4342 (1966) for the definitions of the various structural parameters).

A comparison of the bond angles in Table V shows that the angles increase in the order FPF < FPCl < ClPCl. If the angles determined for PF_2H (FPF = 99.0 ± 0.2°, HPF = 96.3 ± 0.5°)[20] are included in the comparison, it is apparent that as the size of atoms increase (in the order H < F < Cl), the angles increase.

The PF bond distance is slightly larger in PF_2Cl than in PF_3, whereas the PCl distance in PF_2Cl is slightly smaller than the corresponding distance in PCl_3. This increase in the PF and PCl distances with increasing chlorine substitution parallels a corresponding decrease in PF and PCl force constants.[21] Inclusion of the PF distance in PF_2H (1.582 ± 0.002 Å)[20] in the comparison suggests that the bond distances in these molecules increase as the average electronegativity of the substituents decreases.[22]

The asymmetry of the quadrupole coupling constant tensor provides evidence for possible delocalization of p-electron charge density from the chlorine atom to the phosphorus. It was shown above that this asymmetry predicts a minimum π-bond character of 1.5% and corresponding loss of electrons from the p_y orbital of 0.03. Since 0.03 electron lost from p_y is a relatively small number, it is useful to recall the results for vinyl chloride for comparison.[23] In vinyl chloride $\Delta = 9.98$ MHz and the corresponding loss of charge is 0.06 electron. Thus, on the basis of this simple theory, the π-bond character of the CCl bond in vinyl chloride is predicted to be twice that of the PCl bond in PF_2Cl. However, in vinyl chloride it is probable that π_x is small compared to π_y, whereas in PF_2Cl, where all of the phosphorus d orbitals are available for π bonding, loss of electrons due to π bonding can occur from both p_x and the p_y orbitals. It is therefore possible that the π bonding in PF_2Cl is greater than that indicated here.

Acknowledgment.—Advice and encouragement from Professor K. Cohn are gratefully acknowledged.

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