Dipole Moment Studies. VII. Dipole Moments of the Halofluorophosphines

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Dipole moment measurements have been made on a series of halophosphines using gas phase heterodyne beat methods. Values obtained are: PF_3, 1.00 ± 0.03 D; PF_2Cl, 0.93 ± 0.01 D; $PFCl_2$, 0.86 ± 0.05 D; PF_2Br, 0.83 ± 0.05 D; and PF_2I, 0.85 ± 0.06 D. The value for PF_3 is in reasonable agreement with the microwave value [R. G. Schulman et al., Phys. Rev. **78**, 145 (1950)], of 1.025 ± 0.009 D. Molecular moments for the mixed halophosphines are approximated reasonably well by the vector sum of P–X moments, but the value for PF_2H cannot be estimated in this way. An explanation is offered in terms of a polarization model.

In previous papers of this series[1] the best available dipole moment values for alkylphosphines, alkylamines, alkylphosphineboranes, and alkylamineboranes were reported. The results of these studies were satisfactorily rationalized in terms of a polarization model in which a lone pair moment for nitrogen was identified and P–R bond moments were varied systematically in order to compensate for changes in the polarizability of phosphorus as alkyl groups replaced hydrogen. The present study was initiated in order to determine whether the same kinds of variations were indicated in a similar series of halophosphines. One would anticipate that changing one halogen for another would have a smaller effect on phosphorus polarizability than would replacing a hydrogen atom by an alkyl group. If this is true, the concept of bond additivity would be more reliable than would be true when hydrogen is bound to phosphorus. Another factor noted in the alkylphosphine studies was the role of the inductive effect of the R group on the P–R moment. This concept would also be applicable here. Two series were considered. The first was F_3P, F_2PCl, $FPCl_2$, PCl_3. The second was the series F_3P, F_2PCl, F_2PBr, F_2PI. Of these compounds the dipole moments for the mixed halophosphines had not been determined previously. In addition PF_3 was reinvestigated to check our measurements against a previously reported microwave value.[2]

RESULTS

The dipole moments were obtained by the standard Debye method and are recorded in Table I, along with literature values for the unsubstituted trihalophosphines. The relatively large standard error limits for PF_2I and $PFCl_2$ reflect their limited volatility and tendency toward disproportion. In making the measurements, particular care was taken, especially with PF_2I, to assure the purity of the sample at all states of the measurement. It was frequently redistilled and its purity checked by infrared spectroscopy.

The overall molecular moments were resolved into bond moments using the procedures described earlier.[1] It was assumed that the phosphorus lone pair moment was zero and that bond angles had values as shown in the literature[8]: for PF_3, $FPF=98.2°$; for PCl_3, $ClPCl=$

$100°$; for PBr_3, $BrPBr=101°$; and for PI_3, $IPI=100°$. The bond moments were obtained by considering the PX_3 molecular dipole moment as a resultant of three equivalent P–X vectors acting at the angles given above. In carrying out the vector addition of bond moments to obtain molecular moments for PX_2Y, the following angles were used: $FPF=98°$, $FPX=100°$, $XPX=100°$. Changes of 1–2° in these values give changes of about

TABLE I. Dipole moments of halophosphines.

Sample	Molecular μ (observed) (debyes)	Bond μ P–X (calculated) (debyes)	Molecular[a] μ (calculated) (debyes)
PF_3	1.00 ± 0.03	0.70	...
	1.025 ± 0.009[b]		
PF_2Cl	0.93 ± 0.01		0.94
	0.890 ± 0.010[c]		
$PFCl_2$	0.86 ± 0.05		0.90
PCl_3	0.78 ± 0.01[d]	0.57	...
PF_2Br	0.83 ± 0.05		0.89
PBr_3	$0.52+?$[e]	0.37	
PF_2I	0.85 ± 0.05		0.92
PI_3	$0.00\pm?$[f]	0.00	
PF_2H	1.35 ± 0.02[g]		1.09

[a] Calculated as vector sum of bond moments.
[b] Reference 2.
[c] Reference 3.
[d] Reference 4.
[e] Reference 5.
[f] Reference 6.
[g] Reference 7.

0.02 D in the resultant molecular moment. Bond moments are listed in Table I.

DISCUSSION

Inspection of the results given in Table I shows that in every case the simple vector sum of the bond moments falls close to the experimental error limit range. As anticipated, changes of one halogen atom for another seem to have less effect on the polarizability of phos-

TABLE II. Experimental values for determination of dipole moments of gaseous halophosphines.

	T (°K)	$(\Delta C/\Delta P)_{P=0}$ (pF/mm)$\times 10^3$	(P_T) cc		T (°K)	$(\Delta C/\Delta P)_{P=0}$ (pF/mm)$\times 10^3$	cc
PF$_3$	300.29	1.161	33.97	PF$_2$I	298.86	1.500	43.68
	292.03	1.200	34.15		290.29	1.560	44.13
	281.78	1.289	35.39		281.19	1.597	43.76
	273.11	1.360	36.19		274.31	1.665	44.51
	262.97	1.440	36.90		267.10	1.745	45.42
	249.90	1.564	38.09		260.02	1.810	45.86
	245.30	1.600	38.25				

$$P_T = (13.7 \pm 1.2) + (6080 \pm 336)/T \qquad\qquad P_T = (28.7 \pm 3.5) + (4406 \pm 971)/T$$

	T (°K)	$(\Delta C/\Delta P)_{P=0}$	cc		T (°K)		cc
PF$_2$Cl	298.96	1.209	35.21	PFCl$_2$	303.44	1.206	35.66
	287.68	1.278	35.84		292.38	1.268	36.17
	277.54	1.351	36.53		282.99	1.354	37.34
	267.87	1.427	37.25		273.86	1.402	37.42
	258.61	1.500	37.80		265.05	1.471	38.00
	250.19	1.587	38.70		256.59	1.532	38.32

$$P_T = (17.5 \pm 0.5) + (5275 \pm 146)/T \qquad\qquad P_T = (21.0 \pm 2.0) + (4494 \pm 548)/T$$

	T (°K)		cc
PF$_2$Br	298.94	1.328	38.67
	287.88	1.404	39.40
	277.39	1.494	40.37
	267.60	1.542	40.21
	258.74	1.627	41.02
	250.05	1.707	41.06

$$P_T = (24.7 \pm 1.8) + (4424 \pm 500)/T$$

phorus than does the replacement of a hydrogen atom by an alkyl group. Data are consistent with chemical prejudices which indicate that the phosphorus atom should be the positive member in the P–X linkage.

While vector addition gives fairly reasonable values for the halophosphines, it is significant that bond moment addition does *not* reproduce the result for HPF$_2$. The calculated value is 1.09 D; the measured value is 1.35 D. Clearly the P–F bond moment is somewhat larger in HPF$_2$ than in PF$_3$. A reasonable explanation can be obtained from a vector diagram. In PF$_3$ the positive phosphorus atom is symmetrically placed above three negative fluorine atoms to give the following pattern:
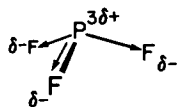
In HPF$_2$ the most logical assumption makes H positive with respect to the phosphorus and fluorine negative with respect to phosphorus. Because the angle between the F–P–F resultant and the P–H vector is nearly 90°

the calculated molecular moment for PF$_2$H is independent of the assumption as to the polarity or direction of the P–H vector.
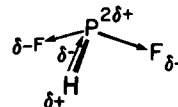
Increased electron density on phosphorus resulting from the H–P vector would permit negative charge movement toward the fluorine atoms thus increasing the magnitude of the P–F vector, a result consistent with the observed values.

As electronegativity arguments would indicate, the P–X moment decreases in the series where X = F, Cl, Br, I, but no quantitative correlation with electronegativity seems justified.[9] In fact that the molecular moment for PF$_2$I is greater than that for PF$_2$Br may seem to be in conflict with the foregoing statement on bond moments. This is not a point of conflict. The pyramidal geometry of the molecules is such that addition of the resultant of the two P–F moments and the negligible P–I moment gives a value equal to or

very slightly larger than addition of the $P-F_2$ resultant and the larger $P-Br$ moment.

EXPERIMENTAL

Materials

Difluorophosphines were prepared according to the literature.[10,11] Cl_2PF was prepared in the same manner from $[(CH_3)_2N]_2PF$ [12] and HCl by the reaction

$$[(CH_3)_2N]_2PF + 4HCl \rightarrow 2(CH_2)_2NH_2Cl + PFCl_2.$$
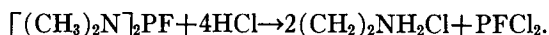
The white solid product was identified as $(CH_3)_2NH_2Cl$ by its x-ray powder pattern. The $PFCl_2$, trapped through vacuum distillation at 126°C, was identified by its vapor density molecular weight: Calc 120.9, Found 118; and its infrared spectrum: 840s, 830s, 520s, 510s. The ^{31}P NMR (40.4 MHz) gave a doublet at $\delta = -220$ ppm from 85% H_3PO_4, $J_{P-F} = 1322$ cps; ^{19}F NMR (94.1 MHz) gave a doublet at $\delta = -20.7$ ppm from F_3CCO_2H, $J_{P-F} = 1315$ cps, in good agreement with the ^{31}P spectrum. Vapor pressure data gave $\log P(\text{mm}) = 8.17 - 1500/T$. PF_3 was obtained from Ozark–Mahoning. All compounds studied were vacuum distilled immediately before use.

NMR data were recorded for neat liquid samples sealed under vacuum in 5 mm tubes using a Varian Associates HA-100 spectrometer. Infrared spectra were recorded on a Perkin–Elmer model 337 spectrometer.

Dielectric constant determinations were made with a heterodyne beat apparatus[7,13] operating at 1 MHz over the temperature range 250–303°K. Capacitance measurements were made over a pressure range of about 60–250 mm and data $(\Delta C/\Delta P)$ were extrapolated to zero pressure to minimize the effects of nonideal behavior. The relatively low temperatures were chosen to minimize disproportionation of the compounds while providing sufficient pressure to allow good precision in the measurements. The cell and system were calibrated with NH_3 and tested with PF_3 as described in Ref. 7.

Experimental data are recorded in Table II. The capacitance data were reduced to molar polarization as $P_T = (760RT/3 \times 273.2C_0) \times (\Delta C/\Delta P)_0$, where C_0 is the capacitance of the evacuated cell, 213.29 ± 0.45 pF. The slope of P_T vs $1/T$ is then related to the dipole moment as $\mu = 0.012812B$ (Debye method).

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