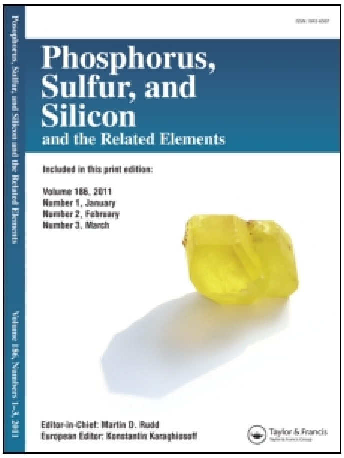

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MOLECULAR AND ELECTRONIC STRUCTURE OF LESS COMMON PHOSPHORUS HALIDES

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Molecular and electronic structures of several known and unknown phosphorus halides are described on the basis of ab initio MO calculations and available experimental data. Trends in bonding and molecular structures have been investigated for the title molecules. Dipole moments and normal mode frequencies are also reported for several molecules in the series.

Key words: Phosphorus halides, electronic structures, dipole moments, photoelectron spectra, molecular geometries.

INTRODUCTION

The properties of phosphorus compounds have been intensively studied during the last decade with investigations focused (amongst other topics) on organophosphorus and transition metal chemistry, phosphorus clusters and compounds containing P=X (X=O, S, Se, Te) functional groups. One specially interesting topic (from quantum chemist's point of view) was the analysis of various stereo-electronic effects[1] induced by large, bulky groups attached to a phosphorus atom. There remains however a body of small (tetra-atomic) phosphorus compounds for which only a few incomplete studies have been reported. The most prominent among these are phosphorus trihalides. Useful summary of theoretical studies performed is given in Table I and was obtained from Quantum Chemistry Literature Data Base published in Journal of Molecular Structure (Theochem). The number of

TABLE I
Number of quantum chemical studies reported recently concerning PX_3(X=H, F, Cl, Br) compounds

	PX_3(X=H,F,Cl,Br) Compounds			
Year	PH_3	PF_3	PCl_3	PBr_3
1984	17	4	4	1
1985	19	4	2	-
1986	15	4	2	1
1987	27	8	1	-
1988	27	5	3	1
1989	14	1	1	-

TABLE II

Molecular geometries, total energies (E_T), dipole moments and enthalpies of formation (g, 298.15 K) for phosphorus halides[a,b]

Molecule (symmetry)	Geometry (pm,deg)	$-E_T$/a.u.	μ/D	ΔH_f^{o}/kJmol^{-1}
PH$_2$F(C$_s$)	r(PF)=160.18 r(PH)=141.78 <HPF=98.1° <HPH=92.6°	441.324323	0.92	-315.8
PHF$_2$(C$_s$)	r(PF)=158.18 r(PH)=141.79 <HPF=96.0° <FPF=97.9°	540.216809	1.35 ∓ 0.02[a] (1.03)	-637.1
PH$_2$Cl(C$_s$)	r(PCl)=205.85 r(PH)=141.55 <HPCl=96.8° <HPH=93.9°	801.372791	0.80	-92.5
PHCl$_2$(C$_s$)	r(PCl)=204.45 r(PH)=141.26 <HPCl=94.9° <ClPCl=103.0°	1260.293442	0.82	-190.5
PHFCl(C$_1$)	r(PF)=158.60 r(PH)=141.54 r(PCl)=204.15 <HPF=96.2° <HPCl=94.6° <ClPF=100.3°	900.253436	0.82	-413.8
PF$_2$Cl(C$_s$)	r(PF)=157.10[a] r(PCl)=203.00[a] <FPCl=99.2° [a] <FPF=97.3° [a]	999.154046	0.93 ∓ 0.01[a] (0.97)	-735.1

TABLE II (*continued*)

Molecule (symmetry)	Geometry (pm,deg)	$-E_T$/a.u.	μ/D	ΔH_f^o/kJmol^{-1}
$PFCl_2(C_s)$	r(PF)=157.43 r(PCl)=203.01 <ClPF=97.7° <ClPCl=101.5°	1359.181829	0.86 ∓ 0.05[a] (0.89)	-511.9
$PH_2Br(C_s)$	r(PBr)=221.85 r(PH)=141.36 <HPBr=97.5° <HPH=92.5°	2911.787766	0.72	-44.9
$PHBr_2(C_s)$	r(PBr)=220.71 r(PH)=140.99 <HPBr=94.4° <BrPBr=111.6°	5481.122354	0.65	-95.4
$PF_2Br(C_s)$	r(PF)=156.99 r(PBr)=219.34 <FPBr=101.2° <FPF=97.0°	3109.565752	0.83 ∓ 0.05[a] (0.90)	-687.6
$PFBr_2(C_s)$	r(PF)=157.71 r(PBr)=219.53 <BrPF=100.5° <BrPBr=106.6°	5580.007551	0.73	-416.7

[a] experimental values from refs.5,11 (values in brackets obtained by vector addition)

[b] 1 a.u.=2625.4 kJ/mol

studies reported decreases with increasing atomic number of halogen substituent and is low when compared with the number of studies reported on phosphine alone. The data available for mixed halides are even scarcer.

The aim of this work is therefore to obtain data on their molecular geometries, stabilities, vibrational frequencies and electronic structures.

Besides these basic parameters we wish to discuss possible trends and changes in molecular properties occurring as a result of varying halogen substitution especially with reference to the phosphorus atom.

DETAILS OF CALCULATIONS

Ab initio MO method implemented in Gaussian 86 and MICROMOL VI packages[2] has been used to obtain molecular properties. The calculations at the Hartree-Fock (HF) level were performed with standard 6-31G** and [6s4p1d] basis sets (for bromine containing molecules). A single polarisation function was added to each atom to increase the basis set flexibility for geometry predictions. The latter basis set has been recently introduced by Binning *et al.*[3] for third row atoms. All geometries were fully optimised and each corresponded to a genuine minimum on the potential energy surface as indicated by the absence of complex values of harmonic vibrational frequencies.

To improve the predicted geometries of unknown phosphorus halides a regression fit of ab initio vs. experimental geometries for PX_3(X=H, F, Cl, Br) series was made and used to obtain values in Table II. In order to account (at least qualitatively) for the correlation energy and to allow direct comparison of photoelectron

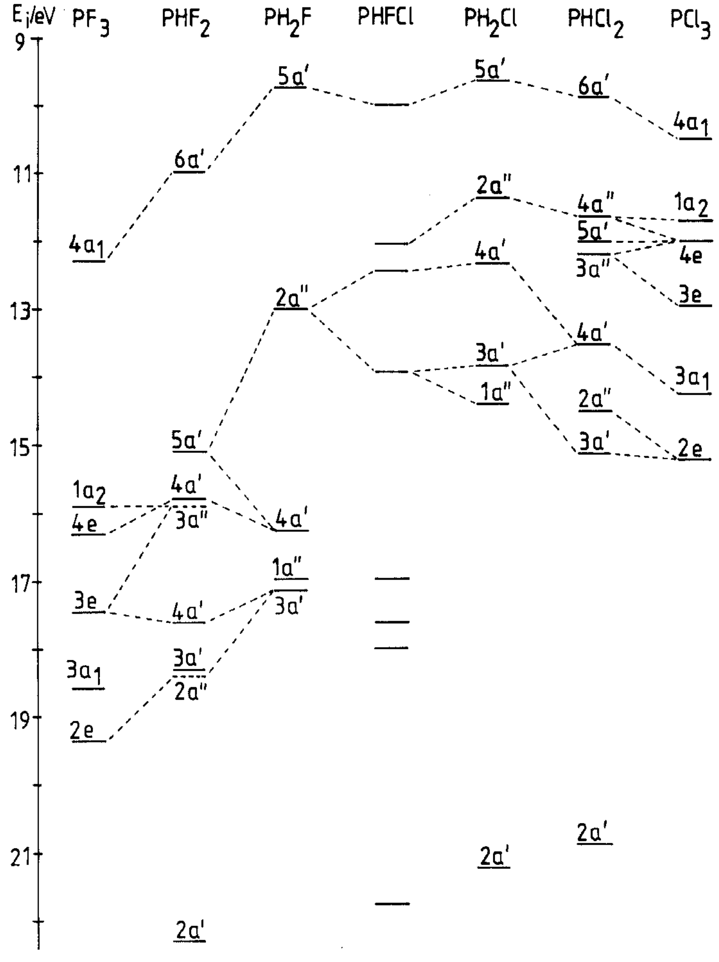

FIGURE 1 Energy level diagram for fluoro- and chlorophosphines.

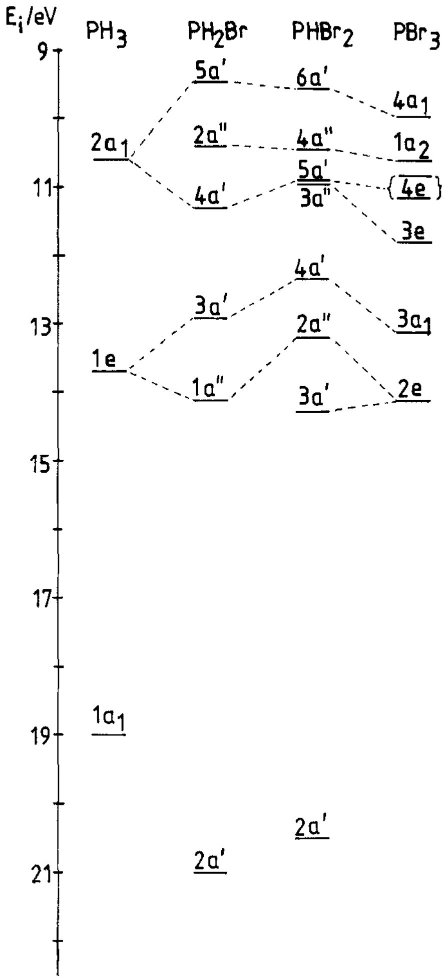

FIGURE 2 Energy level diagram for bromophosphines.

spectra with our results the 92% rule[4] was invoked to correct orbital eigenvalues; the corrected values being shown in Figures 1–3.

The unknown dipole moments were calculated by a vector addition of bond moments and assumed ab initio geometries. The bond moments were obtained from the experimental results reported for several halophosphines.[5] Such empirical approach was adopted in view of the known tendency of ab initio method at HF level to overestimate the magnitude of dipole moments as demonstrated in e.g. phosphorus fluorides.[6]

Standard enthalpies of formation were estimated from bond enthalpies deduced on the basis of experimental data for phosphorus trihalides.[7]

The interpretation of normal modes of vibration was based on the compilation of IR data for phosphorus halides[8] and is intended to help in the identification of possible unknown phosphorus halides (Table III).

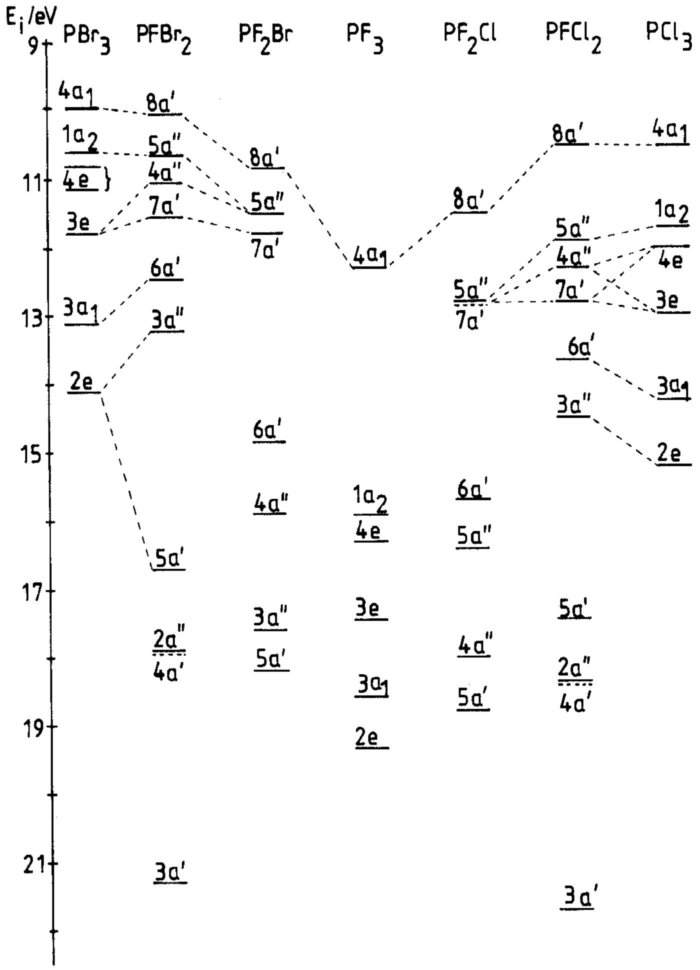

FIGURE 3 Energy level diagram for fluorochloro- and fluorobromophosphines.

RESULTS AND DISCUSSION

The molecular geometries, total energies, dipole moments, enthalpies of formation, vibrational frequencies and corrected binding energies are presented in Tables II–V and Figures 1–3.

The reliability of structural and dipole moment data can be gauged from Tables II and IV where it appears that most HF results are close to or within experimental uncertainty ranges. The results also emphasize the need to obtain more reliable experimental data.

Electronic structure of phosphorus trihalides PX_3(X=F, Cl, Br) has been studied in detail using quantum chemical calculations and photoelectron spectroscopy.[9] For several other phosphorus halides photoelectron spectra have also been reported with tentative band assignments.[10]

TABLE III

Normal modes of vibration in phosphorus halides[a] (X, Y=H, F, Cl, Br)

		Molecule								
Mode		PH_2Cl	$PHCl_2$	PHFCl	PF_2Cl	$PFCl_2$	PH_2Br	$PHBr_2$	PF_2Br	$PFBr_2$
ν_{PX_2}	a'	2305	488		853	505	2316	380	848	417
	a"	2308	495		851	512	2320	403	848	420
ν_{PY}	a'	486	2319	883(P-F) 2308(P-H) 502(P-Cl)	524	840	388	2336	373	831
δ_{YPX}	a'	863	841	956(HPF)	287	259	816	779	236	250
	a"	823	899	825(HPCl) 258(FPCl)	246	315	779	849	215	215
δ_{PX_2}	a'	1103	194		390	192	1100	117	449	120

[a] frequencies (in cm^{-1}) calculated at HF/6-31G** level were scaled by standard factor of 0.893 (ref.12)

TABLE IV

Comparison of experimental and theoretical (HF) geometries for PX_3 series (X=H, F, Cl, Br)

Molecule	Geometrical parameters/pm,deg			
	P-X		<XPX	
	exp.	HF	exp.	HF
PH_3	141.15 ∓ 0.06	141.129	93.32 ∓ 0.02	95.7
PF_3	157.00 ∓ 0.12	156.491	97.8 ∓ 0.2	97.4
PCl_3	204.3 ∓ 0.3	204.820	100.10 ∓ 0.33	100.7
PBr_3	220 ∓ 3	221.993	106 ∓ 3	101.3

TABLE V

Mulliken net atomic charges

Atom	PH_2F	PHF_2	PH_2Cl	$PHCl_2$	$PHFCl$	PF_2Cl	$PFCl_2$	PH_2Br	$PHBr_2$	PF_2Br	$PFBr_2$
P	+0.66	+1.06	+0.35	+0.53	+0.84	+1.17	+0.96	+0.37	+0.60	+1.22	+1.05
H	-0.09	-0.13	-0.02	+0.01	-0.06			-0.02	0.0		
F	-0.49	-0.47			-0.46	-0.43	-0.42			-0.44	-0.45
Cl			-0.32	-0.27	-0.32	-0.31	-0.26				
Br								-0.34	-0.30	-0.35	-0.31

The nature of band at lowest ionization energy in a photoelectron spectrum has been discussed previously.[1] Our results seem to indicate that it corresponds to HOMO with a mixed P 3s, halogen np and H 1s character. Its partial bonding character is least evident in fluorophosphines but even there it seems inappropriate to designate it as a "phosphorus lone pair." The orbitals in ionization energy range 10–13 eV (Figures 1–3) can be attributed to Cl or Br lone pairs and those at even higher energies to P—X or P—H bonding orbitals. Bonding properties of different orbitals, can be deduced from Figures 1–3 where the correlation lines indicate different group orbitals, i.e., halogen lone pairs and phosphorus-halogen bonding orbitals. The main characteristics of electronic structures are: strong interactions between group orbitals (owing to low molecular symmetry) when compared to parent trihalides and the usual binding energy variation with number and type (electronegativity) of halogen substituents.

Our results (within Koopmans' approximation) support the empirical band assignments of photoelectron spectra[10] of PF_2X (X=Cl, Br) compounds and suggest possible ones for not yet prepared phosphorus halides.

The electronic structure variations within the series of compounds studied are also reflected in results of Mulliken population analysis (Table V).

The effect of halogen substitution on phosphorus electron density distribution appears to be generally well correlated with substituent electronegativity, i.e., the larger the number (or electronegativity) of halogen substituents the lower the density on phosphorus. However the depletion of electron density on P atom is not caused solely by electrostatic (Coulombic) forces as indicated in Table V where PF_XBr_y molecules have high P charges comparable to PF_xCl_y ones which contain more electronegative Cl substituents. The reason lies in the increased overlap of

P and Br atomic orbitals which induces charge transfer to otherwise less electronegative Br. If we correlate the net atomic charges with basicities it would appear that fluorobromophosphines should have a basicity comparable to those of fluorochloro analogues.

Similar trends can be seen in bond lengths and angles (Table II). The presence of different halogens in a molecule does not affect the P—H bond length significantly while increased halogenation leads to a reduction in length of all P—X bonds. The least affected is P—F bond which is in keeping with its great stability. Since the molecules are not planar substituents strongly affect bond angles; the larger the substituent the larger the bond angles become.

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