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A LCAO-MO CNDO Study of the Molecular Properties of the Phosphoruspentachlorofluorides

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The authors have studied the geometry and the electronic structure of the pentachlorofluorides of phosphorus(V): PF_5, PF_4Cl, PF_3Cl_2, PF_2Cl_3, $PFCl_4$, and PCl_5 using a CNDO method. Gaussian-type atomic orbital functions are employed. The dipole moments, the bond lengths and angles, the geometries and the electronic structures have been calculated for each molecule and the values found are in good agreement with the available experimental data. The results are coherent for all the molecules and it is found that the five polarisation orbitals of the phosphorus atom play a decisive part in the structure of these compounds.

Introduction

The chlorofluorides of phosphorus V have received little attention with respect to their electronic structure and their geometries are relatively unknown. In particular, only PF_5, PCl_5, and PF_3Cl_2 have been investigated by gas electron diffraction. However, the structure of PF_3Cl_2 has not been definitevely established. Electron diffraction studies indicate a trigonal bipyramidal structure for this compound in which the chlorine atoms assume axial positions. On the other hand, recent spectroscopic investigations using NMR, NQR, infrared and Raman techniques favour a C_{2v} structure wherein the three fluorine atoms occupy one equatorial and the two axial sites.

All other studies of the PCl_nF_{5-n} series, either by LCAO–MO methods or by a normal coordinate analysis are based on bond lengths derived from those of PF_5, PCl_5, and PF_3Cl_2.

In an attempt to clarify the existing contradictions and elucidate the structure of the various pentachlorofluorophosphoranes, we have undertaken a detailed and methodical study of these molecules using an approximate self — consistent MO theory which allows for electron-electron interactions.

Theoretical Part

The CNDO approximation has been described by Pople.[1] In the present paper, we employ a Gaussian-type atomic orbital basis set; such a set allows an effective calculation of the Coulombic repulsion integrals ($3d^2/3d'^2$) and takes into account the five unoccupied 3d-orbitals of the neutral phosphorus atom. Roos and Siegbahn[2] give the coefficients and the exponents of the functions participating in the linear combinations representing the atomic orbitals s and p. To represent the 3d-orbitals, we use, first, a linear combination including 3 gaussian type functions which are substituted for the Slater's function according to Mitchell.[3] This reduced form is obtained using Huzinaga's method.[4]

In order to simplify the calculation, we have used only one suitable gaussian-type function in addition to the three function combination. This modification does not change the results obtained.

In the present work, we have reduced the complexity of the calculations by not considering the 3d orbitals of the chlorine atoms; however, a complete calculation should make allowance for these orbitals.

All calculations have been carried out using a Fortran IV Sesos 3 program written by the authors for IBM/360/44 and 360/65 at the Strasbourg-Cronanbourg «Centre de Recherches Nucléaires».

Results and Discussion

The Pentafluorophosphorane. The structure of this molecule has been determined by electron diffraction.[5,9,10] It consists of a regular trigonal bipyramid in which the three equatorial bond lengths are 1.534 Å and the two axial bond lengths are 1.577 Å.

1. If we consider only the 3s and 3p orbitals of phosphorus, calculations of the molecular energy can be performed using an axial P–F distance of 1.577 Å. The corresponding energy curve attains a minimum (–142.615 a.u.) for an equatorial P–F bond length of 1.72 Å (Figure 1).

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2. If, on the other hand, we consider also the 3d polarisation orbitals on the phosphorus atom, we obtain a lowest energy value of –143.608 a.u. when the equatorial and axial P–F bond lengths are respectively 1.58_7 Å and 1.60_0 Å. The net charges on the different atoms are compared to those proposed by Santry and Segal[6] who used a set of Slater-type atomic orbital functions (Table III).

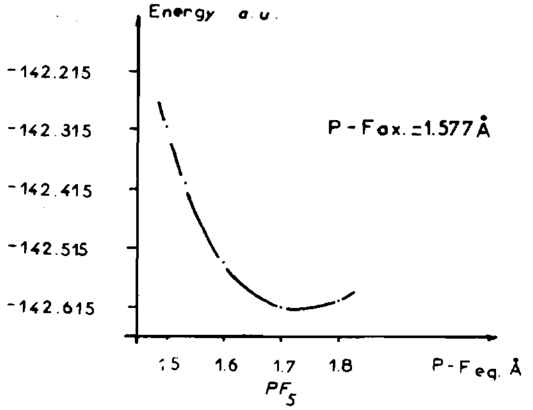

Figure 1.

The molecule PF_5 illustrates the importance of the polarisation orbitals and serves as test for the method employed.

Table I. Molecular Energies of the Isomers.

Molecules	Symmetry	Energies
PF_5	D_{3h}	— 143.608 a.u.
PF_4Cl	C_{2v}	— 134.224 a.u.
	C_{3v}	— 134.206 a.u.
	C_{4v}	— 134.208 a.u.
	C_s	— 134.205 a.u.
PF_3Cl_2	3s, 3p orbitals on the phosphorus atom	
	D_{3h}	— 124.772 a.u.
	3s, 3p and 3d orbitals on the phosphorus atom	
	D_{3h}	— 124.801 a.u.
	C_{2v}	— 124.842 a.u,
PCl_3F_2	D_{3h}	— 115.472 a.u.
	C_{2v}	— 115.416 a.u.
	C_s	— 115.438 a.u.
PCl_4F	C_{3v}	— 106.060 a.u.
	C_{2v}	— 106.030 a.u.
	C_{4v}	— 106.010 a.u.
PCl_5	D_{3h}	— 96.656 a.u.

The Tetrafluorochlorophosphorane. According to Muetterties,[7] we can consider four geometrical isomers for PF_4Cl; these consist of two trigonal bipyramids and two tetragonal pyramids. The single chlorine atom may ocupy either an equatorial or an axial position, or the molecule may have either C_{4v} or C_s symmetry as shown in Figure 2 (1a, 1b, 1c, 1d).

If we assume C_{2v} symmetry for PF_4Cl, with respective equatorial and axial P–F and P–Cl bond lengths of 1.58_7Å, 1.60_6 Å and 1.92_3 Å, the lowest molecular energy is –134.224 a.u.

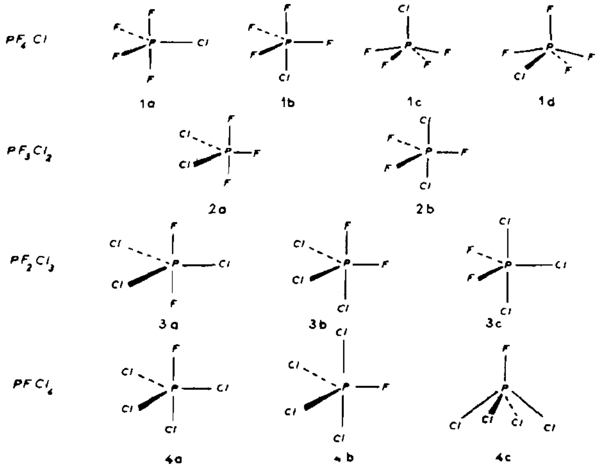

Figure 2.

The energies of the tetragonal isomers with a Cl–P–F bond angle of 103° are higher than for C_{2v} symmetry (Table I). In the same manner, the molecular energy as a function of Cl–P–F bond angle can also be estimated for different values of the P–F bond length in the case of C_{4v} symmetry. It is seen that the energy varies to the extent of 0.005 a.u. in the region of the minimum, when the bond length varies by 0.015 Å. This tendency is confirmed for PF_3Cl_2. The energy differences for the possible isomers of a molecule are at least 0.02 a.u.

Table II. PF_5 Net Charges.

	QP	QFeq.	QFax.
SANTRY	1.13	—0.293	—0.209
AUTHORS	1.28	—0.288	—0.235

Table III.

Molecules	Dipole moment calc.	Dipole moment exptl.
PF_5	0.00	0.00
PF_4Cl	0.89	0.78
PF_3Cl_2	0.91	0.68
PF_2Cl_3	0.00	0.00
$PFCl_4$	0.20	0.21
PCl_5	0.00	0.00

We may therefore conclude that the C_{2v} configuration represents the most stable isomer for PF_4Cl and this is in agreement with the result of infrared and Raman studies carried out by Holmes.[8]

The Trifluorodichlorophosphorane. The bond lengths and angles corresponding to a regular trigonal bipyramid (D_{3h} symmetry) have been determined by gas electron diffraction:[9]

$$r(P—F)=1.59\ Å \quad r(P—Cl)=2.05\ Å; \quad \theta\alpha(F_1—P—F_2)=120° \quad \text{and} \quad \theta\beta(Cl—P—Cl)=180°.$$

1. First, we consider only 3s and 3p orbitals on the phosphorus atom, and the energy is determined as a function of $\theta\alpha$ and $\theta\beta$. Use of the calculated values $\theta\alpha = 140°$ and $\theta\beta = 180°$ heads to the lowest energy. The chlorine atoms are situated in apical positions.

2. The calculations are reported for the case involving 3d phosphorus orbitals. The energy decreases to −124.810 a.u. for the bond angles $\theta\alpha = 179.5°$ and $\theta\beta = 123°$. These results are comparable to those obtained by Bartell and Hansen,[10] in an electron diffraction study of $P(CH_3)_2F_3$ (Figure 3).

The stable isomer for PF_3Cl_2 has C_{2v} symmetry: the fluorine atoms occupy one equatorial and two axial positions in a trigonal bipyramid. Muetterties and co-workers[11] as well as Salthouse and Waddington,[12,14] also propose this model on the basis of NMR and infrared measurements.

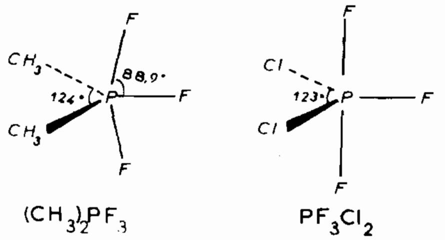

Figure 3.

Assuming the presence of two different fluorine environments and C_{2v} symmetry we may consider the energy with respect to P—Cl and equatorial and axial P—F bond lengths. We obtain a lowest energy value of −124.842 a.u. for the following interatomic distances: P—Feq. = 1.59_2 Å; P—Fax. = 1.61_5 Å; P—Cl = 1.92_4 Å.

Similar calculations for a D_{3h} configuration in PF_3Cl_2 lead to a lowest molecular energy of −124.801 a.u. for the bond lengths: P—F = 1.58_9 Å and P—Cl = 1.95 Å.

It is found that the stable isomer of PF_3Cl_2 must be of C_{2v} symmetry.

The trichlorodifluorophosphorane. Holmes and Gallagher[13] have proposed D_{3h} symmetry (Figures 2, 3a) for PF_2Cl_3. ^{19}F NMR spectra recorded at −15°C indicated that the three chlorine atoms are situated in equatorial positions in a trigonal bipyramid.[13]

The lowest molecular energy is obtained for P—Cl and P—F bond lengths of respectively 1.93_7 Å and 1.61_8 Å. This energy is lower than that of the two other possible trigonal bipyramidal isomers for PF_2Cl_3.

The stable isomer for PF_2Cl_3 has D_{3h} symmetry and this interpretation is in agreement with vibrational, NQR and NMR spectra.[14] Recently, Beattie and co-workers[15] have shown that the Raman spectra obtained for the compound can only be interpreted in terms of D_{3h} symmetry.

The tetrachlorofluorophosphorane. Since positional isomerization is possible in PCl_4F (Figure 2, 4a, b, c), it was expected that the complete infrared and Raman vibrational spectra would be useful in resolving the stereochemical aspects. Towards this end, we studied the molecular energy as a function of the phosphorus-ligand distances. The C_{3v} trigonal bipyramidal structure has the lowest energy when the P—F and the equatorial and the axial P—Cl bond lengths are taken at 1.62_2 Å, 1.94_1 Å, and 1.98_0 Å respectively. The isomer of C_{4v} symmetry (Figure 2, 4c) has been considered briefly. Calculations are carried out with Cl—P—F bond angles of 90°, 100°, 101°, 135°. The tetragonal pyramid with a bond angle of 101° has the lowest energy value (−106.010 a.u.), but this energy is higher than in the case of the trigonal bipyramids (Figures 2, 4a, 4b).

The most stable geometrical isomer of PCl_4F should have C_{3v} symmetry and this is supported by infrared and Raman studies reported by Holmes.[16]

The Pentachlorophosphorane. PCl_5 has been studied by Rouault,[17] who used gas electron diffraction techniques. In the D_{3h} structure found for PCl_5, the equatorial P—Cl bond length is 2.04 Å and the axial bond length is 2.18 Å.

The lowest molecular energy value for PCl_5 is obtained when the equatorial bond length is 1.94_9 Å and the axial length is 1.99_6 Å. These values are 10% lower than those determined by electron diffraction.

The Dipole Moments. We have as certained the stable isomers in the $PF_{5-n}Cl_n$ series with the aid of an approximate self-consistent CNDO—MO theory. The dipole moments have been calculated for each molecule. It is evident from Table III that the values found are in good agreement with the experimental dipole moments.

Electronic Structures of the Pentachlorofluorophosphoranes. The analysis of the molecular wave functions also furnishes the net charges on the different atoms. From Table IV it is seen that the charge

Table IV. $PF_{5-n}Cl_n$ Net Charges.

Molecules	QP	QF eq.	QF ex.	QCl eq.	QCl ax.
PF_5	1.280	−0.235	−0.290	—	—
PF_3Cl_2	1.225	−0.246	−0.313	−0.106	—
PF_4Cl	1.164	−0.255	−0.342	−0.112	—
PF_2Cl_3	1.098	—	−0.368	−0.120	—
$PFCl_4$	1.060	—	−0.378	−0.133	−0.290
PCl_5	1.030	—	—	−0.147	−0.296

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Table V. $PF_{5-n}Cl_n$ Electronic Population in the Valence Orbitals.

	Orbitals	PF_5	PF_4Cl	PF_3Cl_2	PF_2Cl_3	$PFCl_4$	PCl_5
phosphorus	3s	0.932	0.967	0.998	1.027	1.025	1.037
	3p	1.955	2.08	2.21	2.348	2.479	2.62
	3d	0.828	0.727	0.268	0.525	0.429	0.310
eq. fluorine	2s	1.840	1.843	1.845	—	—	—
	2p	5.394	5.400	5.410	—	—	—
ax. fluorine	2s	1.848	1.854	1.860	1.864	1.871	—
	2p	5.440	5.459	5.481	5.504	5.507	—
eq. chlorine	3s	—	1.869	1.869	1.872	1.876	1.880
	3p	—	5.237	5.243	5.248	5.256	5.264
ax. chlorine	3s	—	—	—	—	1.892	1.900
	3p	—	—	—	—	5.396	5.396

(QP) on the phosphorus atom decreases regularly as the number of Cl atoms increases. This is in accord with the difference of electronegativity between fluorine and chlorine. It is also observed that a ligand in axial position has a more negative charge than the same ligand occupying an equatorial site and this may be correlated with the fact that the axial bond lengths are longer than the equatorial ones.

It is interesting to consider the effect on the electronic population in the valence orbitals when a fluorine atom is substituted by a chlorine atom. This effect is especially pronounced in the 3d-phosphorus orbitals in which the population decreases from 0.82 to 0.31 electron. On the 3p orbitals, on the other hand, the population increases from 1.9 to 2.6 (Table V) electrons when the number of Cl atoms increases.

Using these results, we can interpret the nature of the phosphorus-halogen bond. We may presume that σ donation from the phosphorus towards the ligand will be accompanied by back-donation from the $p\pi$ ligand orbitals towards the $d\pi$ phosphorus orbitals. The extent of back-donation appears to decrease progressively as F atoms are replaced by Cl atoms.

Conclusion

In the present work, we have shown that the application of LCAO–MO methods is helpful in the systematic study of a serie of phosphorus chlorofluorides. In particular, it is found that the five polarisation orbitals of the phosphorus atom play a decisive part in the electronic structure of the pentachlorofluorophosphoranes. This requires, in the representation of the atomic orbitals the use of functions allowing an explicit computation of the interactions involved.

Further, it is possible to observe the evolution of the molecular properties, particularly concerning the geometry, the bond lengths and angles, and the dipole moments. The calculated structural features may be summarized as follows:

— The molecules are trigonal bipyramids or distorted trigonal bipyramids;

— Axial phosphorus-ligand bonds are longer than equatorial phosphorus-ligand bonds;

— The splitting (rPF_{ax}–rPF_{eq}) increases with the number of Cl atoms.

— Both P–F and P–Cl bond lengths decrease as the number of F atoms increases;

— The theory of Muetterties which states that the F atoms show a preference for the axial position is confirmed.

The results are coherent for all the molecules of the series, and are in agreement with the conclusions of recent spectroscopic investigations based on NMR, NQR, infrared and Raman techniques. The dipole moments are close to the experimental determined values.

It would appear that only non-empirical *ab initio* LCAO–MO calculations, using an extended basis set give the most precise description of electronic structures. However, a systematic study of the pentachlorofluorophosphoranes series still involves difficulties arising from the complexity and the length of the required calculations.