Non-empirical Valence-shell Self-consistent Field Molecular-orbital Calculations on Group 5 Tri- and Penta-halides

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Non-empirical valence-shell SCFMO calculations have been made on the tri- and penta-fluorides and chlorides of the elements N, P, As, and Sb. The calculations use a minimal basis plus *d* orbitals for the Group 5 atom. The calculated geometries of the trihalides agree well with experimental data. The dissociation energy for the process $MX_5 \longrightarrow MX_3 + 2X$ has been calculated and is negative for NF_5, NCl_5, and $AsCl_5$. Calculations on the mixed phosphorus pentahalides with trigonal-bipyramid structures show that fluorine is energetically preferred in the equatorial positions in all cases.

THERE are many outstanding theoretical problems concerned with the chemistry of heavy main-group elements which have not received attention because of the previous lack of a quantitative valence model which can encompass these elements. Although the similarity of chemical properties is the dominant feature of the periodic classification, there are some puzzling aspects of the differences within a Group. In this paper we consider one example of this, namely the different abilities of the Group 5 elements to extend their co-ordination number from three to five in their halogen compounds.

No pentahalides of nitrogen have been prepared. For the heavier elements, all the pentafluorides are known, but $AsCl_5$ and $BiCl_5$ have not been prepared. Phase studies[1] and other thermodynamic evidence[2] suggest that $AsCl_5$ is unstable with respect to $AsCl_3$ and Cl_2. This difference between the elements P to Bi might appear small, but it is paralleled by some properties of the corresponding elements of other Groups. The elements Ga to Br, which follow the first transition series, and Te to Po, which follow the lanthanide series, show a reluctance to exhibit their maximum valence state.[3]

The object of this paper is to see if a recently developed non-empirical SCFMO scheme, in which only valence electrons are explicitly considered, can provide a satisfactory interpretation of the bonding in such heavy-element compounds. We present calculations on both the geometry and stability of the tri- and penta-fluorides and chlorides of the elements N to Sb. Bismuth was not included in the scheme because we lack a standard program which can handle *f* electrons: this is needed in our method for calculating the potentials of inner electrons of the free atoms. Although the bromides were not included, our method is capable of handling such compounds.

METHOD OF CALCULATION

The method used for these calculations has been described in earlier papers,[4,5] and involves the calculation of approximate valence molecular orbitals without the explicit consideration of core electrons. No empirical parameters were employed, and calculations were carried out by a modification of the all-electron SCFMO ATMOL series of programs. Further details of this procedure have been given in an earlier paper or can be obtained on request to the authors.

The essential features of the method are as follows. (*i*) The valence basis functions are atomic Slater-type orbitals which were orthogonalized in an all-electron calculation to the core eigenfunctions. (*ii*) All one-electron integrals were calculated exactly in terms of this orthogonalized basis. (*iii*) The one-centre nuclear attraction integrals of the molecular calculation were scaled so as to take account of the Hartree–Fock potential of the atomic cores. This penetration correction is determined by the condition that the Fock matrix elements of the all-electron and valence-electron calculations of the atom are the same. (*iv*) The multicentre nuclear-attraction integrals were calculated assuming a nuclear charge of $Z - N_c$, where N_c is the number of neglected core electrons. (*v*) All one-centre two-electron integrals were calculated exactly in terms of the orthogonalized basis. (*vi*) All multicentre two-electron integrals were calculated in terms of the corresponding non-orthogonalized valence Slater-type orbitals.

The majority of the time saved arises from approximation (*vi*), and to some extent from a reduction of the size of the basis in the SCF iterations. The major source of error arises from the lack of orthogonality of the valence basis with the molecular-core eigenfunctions on adjacent atoms, but under most circumstances this does not lead to large deviations from comparable all-electron calculations. However, for short bond lengths such as in N_2 and for orbitals of low exponent,[4,5] the error can be large.

The calculations were made in a minimal basis of Slater orbitals, using Clementi's atomic optimized exponents,[6,7]

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[1] W. F. Smith and J. E. Hora, *J. Amer. Chem. Soc.*, 1904, **26**, 632.

[2] C. J. Adams and A. J. Downs, *J. Inorg. Nuclear Chem.*, 1972, **34**, 1829.

[3] J. E. Huheey, 'Inorganic Chemistry,' Harper and Row, New York, 1972, p. 619.

[4] M. Horn and J. N. Murrell, *J.C.S. Faraday II*, 1974, 769.

[5] J. N. Murrell and I. G. Vincent, *J.C.S. Faraday II*, 1975, 890.

[6] E. Clementi and D. L. Raimondi, *J. Chem. Phys.* 1963, **38**, 2686.

[7] M. L. Unland, J. H. Letcher, and J. R. Van Wazer, *J. Chem. Phys.*, 1969, **50**, 3214.

and these were transformed to a three-gaussian basis for all orbitals. Calculations were also made with valence *d* orbitals of the Group 5 atom added to the minimal basis. As no optimization of *d*-orbital exponents has been made on the heavier members of Group 5, it was decided to take the *d*-orbital exponent to be equal to that of the corresponding *p* orbital in all cases. Experimental geometries for the tri- and penta-halides are listed in Tables 1 and 2, and where experimental geometries are unknown these were estimated by comparison with other known geometries.

TABLE 1

Experimental and calculated geometries of the Group 5 trihalides

	Experimental			Calculated			
				(*s,p,d*) Basis		(*s,p*) Basis	
MX_3 (C_{3v})	Bond length, R/pm	Bond angle, θ/°	Ref.	R/pm	θ/°	R/pm	θ/°
NF_3	136.5	102.37	*a*			136.5	105
PF_3	157.00	97.8	*b*	158	98	177	93
	156.3	96.9	*c*				
	156.0	97.8	*d*				
AsF_3	170.89	95.8	*e*	176	95	183	91
	170.63	96.16	*f*				
SbF_3	187.6	94	*g*	200	93	204	88
	187.9	95	*h*				
	192	87.3	*i*				
NCl_3	175.9	107.1	*j*			189	110
PCl_3	203.9	100.27	*k*	213	102	226	100
	204.3	100.1	*l*				
$AsCl_3$	216.21	98.6	*e*	230	99	234	98
	216.1	98.4	*l*				
$SbCl_3$	232.5	99.5	*m*	250	96	252	94
	236	95.2	*n*				

[a] M. Otake, C. Matsumura, and Y. Morino, *J. Mol. Spectroscopy*, 1968, **28**, 316. [b] Y. Morino, K. Kuchitsu, and T. Moritani, *Inorg. Chem.*, 1969, **8**, 867. [c] E. Hirota and Y. Morino, *J. Mol. Spectroscopy*, 1970, **33**, 460. [d] N. Zumbulyadis and B. P. Dailey, *Mol. Phys.*, 1973, **26**, 777. [e] S. Konaka and M. Kimura, *Bull. Chem. Soc. Japan*, 1970, **43**, 1693. [f] F. B. Clippard and L. S. Bartell, *Inorg. Chem.*, 1970, **9**, 805. [g] T. Ukaji and H. Uchimura, presented to the 22nd Annual Meeting of the Chemical Society of Japan, Tokyo, March 1969. [h] C. Matsumura and H. Takeo, Symposium on Molecular Structure, Fukuoka, 15th October, 1969. [i] A. J. Edwards, *J. Chem. Soc.* (*A*), 1970, 2751. [j] H. B. Buergi, D. Stedman, and L. S. Bartell, *J. Mol. Structure*, 1971, **10**, 31. [k] K. Hedberg and M. Iwasaki, *J. Chem. Phys.*, 1962, **36**, 589. [l] P. Kusliuk and C. H. Townes, *J. Chem. Phys.*, 1950, **18**, 1109. [m] P. Kisliuk and C. H. Townes, *Phys. Rev.*, 1951, **83**, 210. [n] I. Lindqvist and A. Niggli, *J. Inorg. Nuclear Chem.*, 1956, **2**, 345.

TABLE 2

Experimental geometries of Group 5 pentahalides

	Bond length, R/pm		
MX_5 (D_{3h})	Equatorial	Axial	Ref.
NF_5 *	134.5	138.5	
PF_5	153.4	157.7	*a*
AsF_5	165.6	171.1	*b*
SbF_5 *	181	188	
NCl_5 *	174	186	
PCl_5	202	214	*c*
	204	219	*d*
$AsCl_5$ *	214	226	
$SbCl_5$	231	243	*d*
	229	234	*e*

* Geometries have been assumed from known related compounds.

[a] K. W. Hansen and L. S. Bartell, *Inorg. Chem.*, 1965, **4**, 1775. [b] F. B. Clippard and L. S. Bartell, *Inorg. Chem.*, 1970, **9**, 805. [c] G. V. Romanov and V. P. Spiridonov, *J. Struct. Chem.*, 1967, **8**, 131. [d] M. Ronault, *Ann. Physique*, 1940, **14**, 78. [e] S. M. Ohlberg, *J. Amer. Chem. Soc.*, 1959, **81**, 811.

RESULTS AND DISCUSSION

Comparison of All-electron and Valence-electron calculations on PF_3 *and* PCl_3.—All-electron, *ab initio*, and valence-electron calculations for PF_3 and PCl_3 were compared in order to test the ability of the approximate valence-electron method to reproduce the all-electron molecular eigenfunctions and energies of dissociation. Tables 3 and 4 show the calculated orbital energies of PF_3 and PCl_3 using an extended (*s,p,d*) basis and a minimal (*s,p*) basis, respectively. The all-electron results are fairly well reproduced, with the correct ordering of occupied orbitals. Orbital energies of most of the occupied orbitals lie within 0.02 a.u. (0.5 eV)* of the all-electron values, with larger deviations being noted for the orbitals nearest the core and for the highest-energy orbitals. This observation has been made in previous calculations,[5] but it is pleasing to note that our results for heavier molecules are not significantly worse than those of lighter molecules.

TABLE 3

Non-empirical SCFMO calculations on PF_3 using an (*s,p,d*) basis

	Valence orbital energies/a.u.	
Assignment	All-electron	Valence-electron
7*e*	1.086	0.690
6a_1	0.686	0.642
6*e*	0.674	0.671
5a_1	0.523	0.510
5*e*	0.276	0.300
4a_1	−0.342	−0.293
1a_2	−0.504	−0.522
4*e*	−0.521	−0.539
3*e*	−0.577	−0.589
3a_1	−0.652	−0.656
2*e*	−0.661	−0.681
2a_1	−0.796	−0.750
1*e*	−1.557	−1.561
1a_1	−1.615	−1.670

TABLE 4

Non-empirical SCFMO calculations on PCl_3 (minimal basis)

	Valence orbital energies/a.u.	
Assignment	All-electron	Valence-electron
5a_1	0.177	0.179
5*e*	0.166	0.143
4a_1	−0.358	−0.328
4*e*	−0.423	−0.421
a_2	−0.426	−0.423
3*e*	−0.458	−0.461
3a_1	−0.537	−0.551
2*e*	−0.552	−0.569
2a_1	−0.763	−0.695
1*e*	−1.070	−1.070
1a_1	−1.172	−1.243

The energies of dissociation for PF_3 and PCl_3, obtained from these calculations, are shown in Table 5. There is a tendency in such valence-electron calculations for the total binding energy to be underestimated because of the overestimate of the repulsion of the cores (the neglect of

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* 1 a.u. of energy is equal to 4.359 83 aJ; 1 eV ≈ 1.60×10^{-19} J.

overlap of the cores), but we see that the error for PCl_3 is only 1 eV. Such an error will generally be smaller than the correlation-energy errors which arise in the SCF method, and probably smaller than the errors arising from our use of a small orbital basis.

The Role of d *Orbitals*.—Although we have shown that the valence-electron method should give results comparable to those of all-electron calculations, it remains to be established that such calculations (all-electron and valence-electron) give a good representation of the experimental properties of molecules. From Table 6, we see that all-electron estimates of the experimental dissociation energy of PF_3 are sensitive to the basis used. The addition of valence 3*d* orbitals of P to the minimal basis had a large effect on the stabilization of PF_3, relative to separate atoms.

TABLE 5

Calculated energies (a.u.) of $MX_3(g) \longrightarrow M(g) + 3X(g)$ using all-electron (I) and valence-electron methods (II)

PF_3 (*s,p,d*) basis		PCl_3 (*s,p*) basis	
(I)	(II)	(I)	(II)
0.4207	0.3945	0.1150	0.0769

TABLE 6

Experimental and calculated energies (a.u.) of $PF_3(g) \longrightarrow P(g) + 3F(g)$

Expt.*	All-electron (*s,p,d*) basis	All-electron (*s,p*) basis
0.5777	0.4207	0.0314

* D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, Selected Values of Chemical Thermodynamic Properties, Nat. Bur. Stand. Tech. Note 270–3, U.S. Government Printing Office, Washington, D.C., 1968; A. J. Head, J. B. Pedley, A. Kirk, S. Seilman, and L. G. Heath, Computer Analysis of Thermochemical Data, School of Molecular Sciences, University of Sussex, September 1972.

The importance of valence 3*d* orbitals on the Cl atom was investigated in calculations on NCl_3. It was found that 3*d* orbitals stabilized NCl_3 by only 0.09 a.u, which is only a quarter of the result found by including phosphorus 3*d* orbitals in the PF_3 calculation. We therefore feel justified in taking only valence *s* and *p* orbitals for the halogen, particularly as integrals involving *d* orbitals are time consuming, and if *d* orbitals were included for all atoms the time saved by ignoring the core electrons would be relatively small in comparison.

Geometry of the Trihalides.—The results of valence calculations in which the geometries of the trihalides were optimized are shown in Table 1. For both the fluorides and trichlorides the trends in bond length and bond angle were correctly predicted using either the minimal or extended basis set, but the absolute geometries, and in particular the bond lengths, were much better with the (*s,p,d*) basis. For the heaviest compound, $SbCl_3$, the calculations still overestimated the bond lengths by 20 pm. The geometry and dissociation-energy results show that the inclusion of valence *d* orbitals of the Group 5 element in the molecular minimal basis is necessary for the reliable prediction of experimental properties. Thus, in the following work, (*s,p,d*) basis sets have been used in all cases, except for the nitrogen compounds.

Dissociation Energies of the Tri- and Penta-halides.—In Tables 7 and 8 we show the calculated and experimental energies of tri- and penta-halides relative to the separate atoms. Experimental geometries were adopted for these calculations, and where several experimental estimates exist the average of these was taken. A trigonal-bipyramidal shape was assumed for the non-existent pentahalides, and for SbF_5, and the bond lengths were estimated by comparison with the known pentahalides. Experimental values of the heat of vaporization of NCl_3, and the heat of sublimation of SbF_3, have not been obtained, and the experimental values listed for the dissociation energies of NCl_3 and SbF_3 in Table 7, which neglect these factors, will therefore be overestimates. The calculated dissociation energies are reasonably close to the experimental values, except for NF_3 and NCl_3. We believe that the poor results for NF_3 and NCl_3 are due primarily to the neglect of correlation energy.[8]

TABLE 7

Experimental and calculated energies of dissociation (a.u.) for $MX_3(g) \longrightarrow M(g) + 3X(g)$

Compound	Experimental *	Calculated
NF_3	0.3215	0.0455
PF_3	0.5777	0.3945
AsF_3	0.5584	0.1933
SbF_3	0.5410 †	0.2362
NCl_3	0.2319 †	−0.0814
PCl_3	0.3698	0.2566
$AsCl_3$	0.3537	0.1704
$SbCl_3$	0.3595	0.2630

* See footnote to Table 6. † Estimated values.

TABLE 8

Experimental and calculated energies of dissociation (a.u.) for $MX_5(g) \longrightarrow M(g) + 5X(g)$

Compound	Experimental *	Calculated
NF_5	†	−0.2678
PF_5	0.8814	0.7104
AsF_5	0.7403	0.2407
SbF_5	0.7234	0.3654
NCl_5	†	−0.6934
PCl_5	0.4961	0.3425
$AsCl_5$	†	0.1441
$SbCl_5$	0.4830	0.4019

* See footnote to Table 6; N. Bartlett, 'Chemistry in Canada,' in Chemical Institute of Canada, August 1963, p. 33; P. A. G. O'Hare and W. N. Hubbard, *J. Phys. Chem.*, 1965, **69**, 4358. † Unstable.

From the dissociation energies in Tables 7 and 8, we calculated the energies of the reactions (1) as shown in

$$MX_5(g) \longrightarrow MX_3(g) + 2X(g) \qquad (1)$$

Table 9. These reactions were preferred to (2) as it is

$$MX_5(g) \longrightarrow MX_3(g) + X_2(g) \qquad (2)$$

well known that the Hartree–Fock SCF estimate of the binding energy of the halides involves large correlation-

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[8] E. Clementi, D. L. Raimondi, and W. P. Reinhardt, *J. Chem. Phys.*, 1967, **47**, 1300.

energy errors, particularly for F_2.[9] It is pleasing to see that we calculate an exothermic process for the three species NF_5, NCl_5, and $AsCl_5$, which are unknown. For the stable pentahalides we have fairly good agreement between calculated and experimental energies of reaction, considering the errors arising from the approximate method, neglect of correlation energy, and the uncertainties in geometry.

TABLE 9

Experimental and calculated energies (a.u.) for $MX_5(g) \longrightarrow MX_3(g) + 2X(g)$

MX_5	Experimental	Calculated
NF_5		−0.3133
PF_5	0.3037	0.3159
AsF_5	0.1819	0.0474
SbF_5	0.1824 *	0.1292
NCl_5		−0.6120
PCl_5	0.1263	0.0859
$AsCl_5$		−0.0263
$SbCl_5$	0.1235	0.1389

* Plus $\Delta H_{sub}^{\ominus}$ (SbF_3).

Several suggestions have been put forward for the nonexistence of $AsCl_5$. Amongst these, Dasent[10] has suggested that the 4*s* electron pair of As is bound firmly because of the weak screening of the inner 3*d* orbitals, and, if $AsCl_5$ is to be formed, the 4*s* pair needs to be uncoupled. This promotion energy is high and is reflected in the unusually large difference between the third and fourth ionization potentials of As compared to those of P and Sb.[11] The Cl atom is not electronegative enough to effect this promotion, but the more electronegative F atom can facilitate this, thus explaining the stability of AsF_5.

Examination of the results of our atomic and molecular calculations can be shown to be in agreement with Dasent's conclusions. Table 10 lists the valence *s* and *p* energies of P, As, and Sb, obtained from valence atomic calculations with both a minimal and an (*s*,*p*,*d*) basis. The *d* orbitals influence the *s*- and *p*-orbital energies of As and Sb through their effect on the inner *d* orbitals and hence on the shielding of the nucleus by the core electrons. The addition of *d* orbitals in the case of As is seen to produce a non-monotonic sequence for the *s*- and *p*-orbital energies of the series. This result is not obtained with a minimal basis, and we find that a minimal basis, as well as predicting poor relative stabilities of the pentahalides, does not predict the anomalous stability of $AsCl_5$.

TABLE 10

Atomic valence-orbital energies (a.u.) for Group 5 calculated using the H_3 one-electron Fock operator of the ATMOL method

	(*s*,*p*) Basis		(*s*,*p*,*d*) Basis	
Element	*s*	*p*	*s*	*p*
P	−0.4915	0.1502	−0.4915	0.1502
As	−0.4533	0.1381	−0.5323	0.0853
Sb	−0.3554	0.1284	−0.4010	0.0968

One further feature of the calculation is unusual for $AsCl_5$. Inclusion of valence *d* orbitals in the basis sets of the pentafluorides stabilizes all the occupied molecular orbitals, thus increasing the strength of the bonding. For the pentachlorides, the *d* orbitals have varying effects, and, in particular, the highest-occupied molecular orbital, a M–Cl axial bonding molecular orbital, is stabilized by 0.04 and 0.01 a.u. for PCl_5 and $SbCl_5$, but destabilized by 0.02 a.u. for $AsCl_5$. A Mulliken analysis of the overlap population between M (= P, As, or Sb) and Cl (axial) shows that the axial-overlap population is increased by 0.13 in both PCl_5 and $SbCl_5$ by the addition of *d* orbitals, but only by 0.04 in $AsCl_5$.

Ionization Potentials.—Estimates of the first ionization potential of the Group 5 halides, deduced using Koopmans' theorem, are listed in Table 11, together with the corresponding experimental values. Although absolute values are not accurately predicted, the trends are fairly well reproduced within the trifluoride and trichloride series.

TABLE 11

Experimental and calculated first ionization potentials (eV) of the Group 5 halides

	Experimental	Ref.	Calculated
NF_3	13.73	*a*, *b*	10.31
	13.18	*c*	
PF_3	12.29	*a*	7.97
	12.27	*b*, *d*	
	11.72	*c*	
AsF_3	12.84	*c*	8.90
	13.00	*b*	
SbF_3	12.61	*c*	8.00
NCl_3	10.7	*b*	9.80
PCl_3	10.52	*b*	8.41
$AsCl_3$	10.89	*b*	9.09
	11.7	*e*	
$SbCl_3$			8.54
PF_5			13.33
AsF_5			12.35
SbF_5			12.38
PCl_5			10.07
$SbCl_5$			10.97

[a] P. J. Bassett and D. R. Lloyd, *J.C.S. Dalton*, 1972, 248. [b] J. Müller and K. Fenderl, *Chem. Ber.*, 1971, **104**, 2207. [c] J. P. Maier and D. W. Turner, *J.C.S. Faraday II*, 1972, 711. [d] A. W. Potts, H. J. Lempka, D. G. Streets, and W. C. Price, *Phil. Trans. Roy. Soc.*, 1970, **A268**, 59. [e] W. R. Cullen and D. C. Frost, *Canad. J. Chem.*, 1962, **40**, 390.

Stereochemistry of the Phosphorus Mixed Pentahalides.—The stability of the various isomers of the phosphorus mixed pentahalides, $PCl_{5-n}F_n$ (n = 1—4), has been treated by the semiempirical CNDO method,[12] but no non-empirical study has been reported. No structural parameters exist for the compounds PCl_4F, PCl_3F_2, PCl_2F_3, and $PClF_4$, but i.r. and Raman,[13,14] dielectric,[14,15] and quadrupole and n.m.r.[16] measurements have shown

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[9] G. Das and A. C. Wahl, *J. Chem. Phys.*, 1972, **56**, 3532.

[10] W. E. Dasent, *J. Chem. Educ.*, 1963, **40**, 130.

[11] R. S. Nyholm, *Proc. Chem. Soc.*, 1961, 273.

[12] C. Brun, F. Choplin, and G. Kaufmann, *Inorg. Chim. Acta*, 1972, **7**, 77.

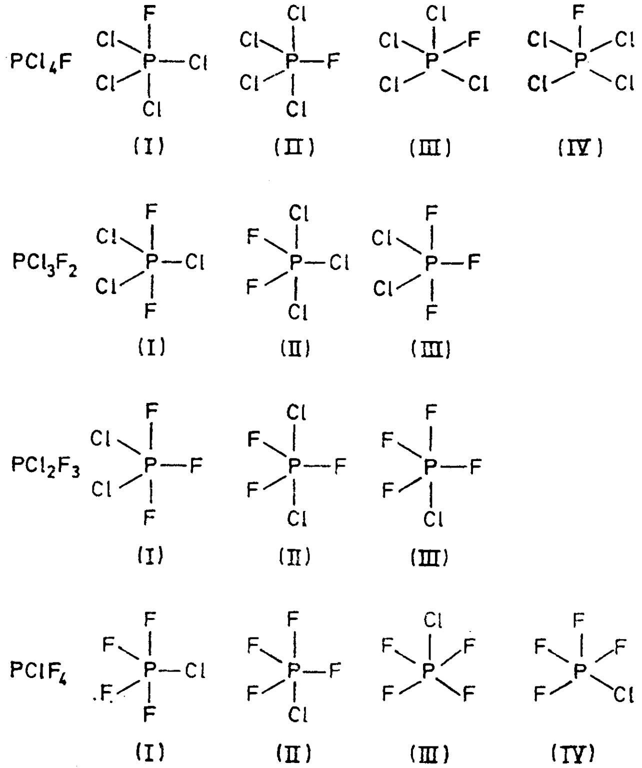
[13] J. E. Griffiths, R. P. Carter, and R. R. Holmes, *J. Chem. Phys.*, 1964, **3**, 863.

[14] R. R. Holmes, *J. Chem. Phys.*, 1967, **46**, 3719

[15] R. R. Holmes and R. P. Carter, *J. Chem. Phys.*, 1965, **43**, 1645.

[16] R. R. Holmes, R. P. Carter, and G. E. Peterson, *Inorg. Chem.*, 1964, **3**, 1748.

that these species have a trigonal-bipyramidal shape with the F atoms preferring the axial positions. An earlier *X*-ray study of PCl_2F_3 [17] indicated a D_{3h} symmetry for this compound, but more recent low-temperature ^{19}F n.m.r. studies [18,19] showed that there are two distinct F atoms in PCl_2F_3 at temperatures below −115 °C, implying a C_{2v} symmetry. At temperatures above −115 °C, F exchange occurs.



Isomers of $PCl_{5-n}F_n$ (n = 1—4)

The possible isomeric forms which exist for the mixed phosphorus pentahalides are shown opposite, and in each case structure (I) is the stable form as indicated by experiment. In our calculations, we assumed bond lengths to be the same as those in PF_5 and PCl_5, namely P-F(eq.) = 153.4, P-F(ax.) = 157.7, P-Cl(eq.) = 202, and P-Cl(ax.) = 214 pm. The results of these calculations are shown in Table 12, where the energy of each isomer is listed relative to isomer (I). It can be seen that in all cases structure (I) is correctly predicted to have the lowest energy. In some cases, the energy difference between (I) and (II) is very small, but it was found that optimization of the Cl(eq.)-P-Cl(eq.) bond angle in PCl_2F_3 (I), and the F(eq.)-P-F(eq.) bond angle in PCl_3F_2 (II), made no significant alteration to the energy difference.

TABLE 12

Relative energies (a.u.) of the isomers of $PCl_{5-n}F_n$ (n = 1—4)

Compound \ Isomer	(I)	(II)	(III)	(IV)
PCl_4F	0	0.0070	0.1228	0.1354
PCl_3F_2	0	0.0157	0.0167	
PCl_2F_3	0	0.0001	0.0092	
$PClF_4$	0	0.0013	0.0657	0.0804

Conclusion.—These calculations, which include the first non-empirical SCFMO calculations on a molecule like $SbCl_5$, give a very satisfactory interpretation of structure, orbital energies, and total energies. The agreement between calculation and experiment is certainly as good as one could expect from equivalent all-electron *ab initio* SCFMO calculations.

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[18] E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, 1963, **2**, 613.

[19] E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, *Inorg. Chem.*, 1964, **3**, 1298.