Ab initio Calculations of the Bonding in Phosphorus Trichloride, Phosphorus Oxide Trichloride, and Phosphorus Sulphide Trifluoride

By **I. H. Hillier** * and **V. R. Saunders**, Department of Chemistry, The University, Manchester M13 9PL

Ab initio SCF–MO calculations of PF_3S, PCl_3, and PCl_3O are described. The importance of 3*d* orbitals on the second row atoms is investigated, and the nature of the bonding compared with that calculated for other co-ordinated phosphines.

THE nature of the bonding in phosphine, the substituted phosphines PF_3 and PMe_3,[1] and the simple complexes involving co-ordination of an oxygen atom or borane group,[2,3] have been studied by *ab initio* self-consistent field molecular orbital (SCF–MO) calculations. These calculations show that the mode of co-ordination can be interpreted in terms of σ-donation from the phosphine and π-acceptance by the phosphine, the latter being critically dependent upon the nature of the co-ordinating group. Both the oxygen atom and borane group act as σ-acceptors, but only oxygen acts as a π-donor, to yield an appreciable π component to the P–O bond, this bond involving to a large extent the phosphorus d_π orbitals.

In this paper we extend our previous studies[1,2] to investigate the co-ordination of a second row element to a substituted phosphine by reporting the results of calculations of phosphorus sulphide trifluoride (PF_3S) and the bonding and mode of co-ordination of phosphine substituted with a second row element by reporting calculations on phosphorus trichloride (PCl_3) and phosphorus oxide trichloride ($POCl_3$).

COMPUTATION

The calculations reported here are all-electron *ab initio* self-consistent field molecular orbital calculations using a basis of Slater type orbitals (STO), except for the fluorine 2*p* orbital where an atomic orbital (AO) was used. The exponents of the STO except for that of the phosphorus 3*d* were the best atom values of Clementi and Raimondi.[4] The importance of 3*d* orbitals in the bonding in molecules containing second-row elements has been shown previously.[1-3]

For PF_3S a phosphorus 3*d* exponent of 1·77, the optimum value in PF_3 was taken, a value of 1·8 being used for the phosphorus 3*d* exponent in PCl_3 and $POCl_3$. To investigate the relative importance of sulphur and phosphorus 3*d* orbitals in PF_3S calculations were performed with sulphur 3*d* orbitals (exponent 1·5) as well as phosphorus 3*d* orbitals in the basis. Integral evaluation was accomplished by expanding each STO in three Gaussian type functions[5,6] (GTF) and the AO in four such functions[7] by the least-squares procedure. Polarization and expansion or contraction of the 3*d* orbitals was included in some calculations as previously described[1] by allowing the relative contribution of the most diffuse *d* GTF to be determined during the self-consistent field procedure (*s*, *p* + split *d* basis). The calculations were performed using the ATMOL system

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[1] I. H. Hillier and V. R. Saunders, *Trans. Faraday Soc.*, 1970, **66**, 2401.

[2] I. H. Hillier and V. R. Saunders, *J. Chem. Soc.* (*A*), 1970, 2475; 1971, 664.

[3] J. Demuynck and A. Veillard, *Chem. Comm.*, 1970, 873.

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

[5] W. J. Hehre, R. F. Stewart, and J. A. Pople, ' Symposium of the Faraday Society,' 1968, **2**, 15.

[6] I. H. Hillier and V. R. Saunders, *Internat. J. Quantum Chem.*, 1970, **4**, 203.

[7] R. F. Stewart, *J. Chem. Phys.*, 1969, **50**, 2485.

of programs on the ATLAS computers of Manchester University and the S.R.C. Atlas Computer Laboratory.

The molecular geometries used are given in Table 1.

TABLE 1

Molecular geometries; bond lengths (Å) and angles (°)

PCl_3	P–Cl	1·99	Cl–P–Cl	103·5
PCl_3O	P–Cl	1·99	Cl–P–Cl	103·5
	P–O	1·45		
PF_3S	P–F	1·538	F–P–F	99·8
	P–S	1·87		

To reduce computational time, the P–Cl bond length and Cl–P–Cl angle in PCl_3 were taken to be the same as those in $POCl_3$.[8] Also, the geometry of the PF_3 group in PF_3S was taken to be the same as in $PF_3{\cdot}BH_3$, thus allowing previously computed molecular integrals to be used in this work. Such small deviations from the experimental geometries are not expected to alter the description of the bonding in the molecules presented here.

RESULTS

The results of the calculations are summarized in Tables 2—7. We first discuss the calculation of PF_3S designed to assess the importance of $3d$ functions on the phosphorus and sulphur atoms. The molecular energies and dipole moments for a number of calculations differing in the degree of inclusion of $3d$ functions are shown in Table 2. In the calculation which gave the lowest molecular energy, $3d$ functions were included on both second row atoms, polarization and expansion or contraction of those on the

TABLE 2

Calculated molecular energies (a.u.) and calculated and experimental dipole moments (D)

		Dipole moment		
			Calculated	
Molecule	Molecular energy	Experimental	Magnitude	Direction
PCl_3	−1701·4982	0·8	0·31	P^+–Cl^-
PCl_3O	−1775·3822	2·4	1·25	P^+–O^-
PF_3S	−1025·9594 [a]		1·05	P^-–S^+
	−1025·9395 [b]		0·18	P^-–S^+
	−1025·6411 [c]	0·63	1·12	P^-–S^+
	−1025·9823 [d]		1·04	P^-–S^+
	−1025·5586 [e]		0·42	P^+–S^-

[a] Sulphur *d*, phosphorus *d* orbitals. [b] No sulphur *d*, phosphorus split *d* orbitals. [c] Sulphur *d*, no phosphorus *d* orbitals. [d] Sulphur *d*, phosphorus split *d* orbitals. [e] No *d* orbitals.

TABLE 3

Orbital populations

		PF_3	PF_3S	PCl_3	PCl_3O
Phosphorus	$3s$	1·51	0·96	1·69	1·19
	$3p(a_1)$	1·05	0·78	1·32	0·76
	$3p(e)$	0·83	1·20	1·46	1·78
	$3d(a_1)$	0·14	0·18	0·07	0·16
	$3d(e)$	0·52	0·83	0·42	0·91
Atomic charge		1·02	1·16	0·10	0·25
Fluorine	$2s$	1·91	1·91		
	$2p$	5·43	5·41		
Atomic charge		−0·34	−0·32		
Sulphur	$3s$		1·81		
	$3p(a_1)$		1·04		
	$3p(e)$		3·24		
	$3d(a_1)$		0·05		
	$3d(e)$		0·06		
Atomic charge			−0·20		
Chlorine	$3s$			1·91	1·91
	$3p$			5·14	5·12
Atomic charge				−0·03	−0·01
Oxygen	$2s$				1·86
	$2p(a_1)$				1·36
	$2p(e)$				3·00
Atomic charge					−0·21

TABLE 4

Overlap populations

(*a*) PF_3S

Phosphorus orbital	Sulphur orbital	
$3s$	$3s$	−0·065
$3s$	$3p_\sigma$	0·347
$3s$	$3d_\sigma$	0·059
$3p_\sigma$	$3s$	−0·037
$3p_\sigma$	$3p_\sigma$	0·327
$3p_\sigma$	$3d_\sigma$	0·025
$3d_\sigma$	$3s$	0·017
$3d_\sigma$	$3p_\sigma$	0·051
$3d_\sigma$	$3d_\sigma$	0·003
$3p_\pi$	$3p_\pi$	0·357
$3p_\pi$	$3d_\pi$	0·050
$3d_\pi$	$3p_\pi$	0·282
$3d_\pi$	$3d_\pi$	0·032

(*b*) PCl_3O

Phosphorus orbital	Oxygen orbital	
$3s$	$2s$	−0·139
$3s$	$2p_\sigma$	0·256
$3p_\sigma$	$2s$	−0·092
$3p_\sigma$	$2p_\sigma$	0·292
$3d_\sigma$	$2s$	0·039
$3d_\sigma$	$2p_\sigma$	0·054
$3p_\pi$	$2p_\pi$	0·378
$3d_\pi$	$2p_\pi$	0·414

TABLE 5

Valence molecular orbitals of PF_3S

		Orbital form (%)							
	Orbital energy	Phosphorus orbital			Fluorine orbital		Sulphur orbital		
Symmetry	(a.u.)	$3s$	$3p$	$3d$	$2s$	$2p$	$3s$	$3p$	$3d$
$8e$	−0·3951		7	7		1		79	1
$12a_1$	−0·5401	8	10	2		4	20	45	2
$1a_2$	−0·6809					33			
$7e$	−0·6985			3		32			
$6e$	−0·7481		1	6		31			
$11a_1$	−0·7705	1	1	6		26	13	1	
$5e$	−0·8152		13	1	2	26			
$10a_1$	−0·8850	4	12		3	20	15		
$9a_1$	−1·0240	24	10	1	2	4	43	4	1
$4e$	−1·6603		6	3	29	1			
$8a_1$	−1·7242	11	3		27	2			

TABLE 6

Valence molecular orbitals of PCl_3

		Orbital form (%)				
	Orbital energy	Phosphorus orbital			Chlorine orbital	
Symmetry	(a.u.)	$3s$	$3p$	$3d$	$3s$	$3p$
$11a_1$	−0·3382	14	32	2		17
$2a_2$	−0·4232					33
$10e$	−0·4315			2		32
$9e$	−0·4715		1	5		31
$10a_1$	−0·5431	3	29	2		21
$8e$	−0·5655		25	1	3	22
$9a_1$	−0·7419	41			10	9
$7e$	−1·0789		9	2	29	
$8a_1$	−1·1691	26	3		22	2

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[8] L. E. Sutton, *Chem. Soc. Special Publ.*, No. 11, 1958.

phosphorus atom being allowed (sulphur *d*, phosphorus split *d*). A Mulliken analysis (Table 3) * yielded a phosphorus 3*d* orbital population (1·01) far in excess of the sulphur 3*d* population (0·11). This indicates that in this molecule 3*d* functions on the sulphur atom do not participate to any appreciable extent in the P–S bond but merely act as polarization functions. In contrast, the large phosphorus 3*d* population indicates that these functions are important in describing the bonding in the molecule. This view is substantiated by the contributions to the bond overlap populations (Table 4) where the 3*d* sulphur orbitals do not contribute significantly to the P–S overlap populations whilst there is an appreciable term involving the phosphorus $3d_\pi$ and sulphur $3p_\pi$ orbitals. The minor contribution of the sulphur 3*d* function to the bonding is further exemplified by the small increase (0·04 a.u.) in the molecular energy when the calculation is repeated in the absence of such functions. However, the polarization effect of sulphur 3*d* orbitals is shown by the considerable change (*ca.* 1 D) in the calculated dipole moment when they are not included in the calculation. The calculation without phosphorus 3*d* orbitals (but with sulphur 3*d* orbitals) gives a molecular energy greater by 0·3 a.u. than that from the calculation including phosphorus split 3*d* functions, again showing the importance of the latter in describing the bonding in this molecule.

TABLE 7

Valence molecular orbitals of PCl_3O

		Orbital form (%)						
	Orbital energy	Phosphorus orbital			Chlorine orbital		Oxygen orbital	
Symmetry	(a.u.)	3*s*	3*p*	3*d*	3*s*	3*p*	2*s*	2*p*
11*e*	−0·4226		1	4		18		40
$2a_2$	−0·4380					33		
10*e*	−0·4540			8		26		11
$13a_1$	−0·4727			5		22	3	24
9*e*	−0·4972			8		27		10
$12a_1$	−0·5713	1	19			12	10	33
8*e*	−0·6120		32		3	15		14
$11a_1$	−0·7370	28	2		9	10	6	6
7*e*	−1·0964		10	2	29			
$10a_1$	−1·1678	13	9	1	22	1	7	
$9a_1$	−1·3539	18	5	2	1		67	4

The orbital populations of Table 3 show that the main change in electron distribution on formation of the P–S bond is a large decrease (0·8 e) in the population of the phosphorus 3*s* and $3p_\sigma$ orbitals and a corresponding increase (0·7 e) in that of the $3p_\pi$ and $3d_\pi$ orbitals. The net result of these two effects combined with the small change in the occupancy of the fluorine orbitals is to increase the charge on the phosphorus atom from 1·02 in PF_3 to 1·16 in PF_3S. An analysis of the valence molecular orbitals of PF_3S in terms of the atomic orbital components is shown in Table 5. The highest filled orbital (8*e*) is predominantly localized on the sulphur atom, but contributes to the P–S π bond. The next orbital ($12a_1$) which correlates with the ' lone pair ' orbital ($8a_1$) of PF_3 is calculated to be 20% localized on the phosphorus atom compared with the corresponding value of 70% in PF_3. The $1a_2$, 7*e*, and 6*e* molecular orbitals are predominantly fluorine 2*p* non-bonding orbitals although they provide contributions to the phosphorus–fluorine bonds involving the phosphorus 3*d* orbitals. The remaining valence molecular orbitals are delocalized and contribute further to the phosphorus–fluorine and phosphorus–sulphur bonds.

We turn now to a discussion of the bonding in PCl_3 and $POCl_3$. The calculated charge distribution in PCl_3 (Table 3) predicts the P–Cl bonds to be only slightly polar with a small net negative charge on the chlorine atoms compared with the large net negative charge (−0·34) on the fluorine atoms in PF_3. The phosphorus 3*d* population (0·5 e) is rather smaller than that calculated in PF_3. The highest filled orbital of PCl_3, $11a_1$, has 48% phosphorus character (Table 6), lower than that of the lone pair orbital in PF_3. The next three orbitals $2a_2$, 10*e*, and 9*e* are predominantly non-bonding chlorine 3*p* orbitals, the remaining valence orbitals contributing to the phosphorus–chlorine bonds. The major changes in the charge distribution on formation of $POCl_3$ are a large decrease (1·06 e) in the population of the phosphorus 3*s* and $3p_\sigma$ orbitals and a large increase (0·81 e) in that of the phosphorus $3p_\pi$ and $3d_\pi$ orbitals, resulting in a net increase of the formal phosphorus charge to +0·25. As in PF_3O,[2] the major contribution to the phosphorus–oxygen bond overlap population (Table 4) is a σ component involving the phosphorus 3*s* and $3p_\sigma$ and oxygen $2p_\sigma$ orbitals, and a π component involving the phosphorus $3p_\pi$ and $3d_\pi$ and oxygen $2p_\pi$ orbitals. The highest filled orbital of $POCl_3$, 11*e*, is mainly non-bonding involving the chlorine 3*p* and oxygen 2*p* orbitals (Table 7). The major contributions to the $2a_2$, 10*e*, $13a_1$, and 9*e* molecular orbitals are chlorine 3*p* orbitals, although the 10*e* and 9*e* contribute to the phosphorus $3d_\pi$–oxygen $2p_\pi$ overlap population. The $12a_1$ orbital is the highest to have significant phosphorus σ component, and is strongly P–O bonding, so that it may be correlated with the ' lone-pair ' donor orbital ($11a_1$) in PCl_3.

DISCUSSION

The bonding in PF_3S is found to be similar to that calculated for PF_3O. The P–S bond has σ and π components, the latter involving to a large extent the phosphorus 3*d* orbitals. Although such functions are important on the phosphorus atom they are found to be relatively unimportant on the sulphur atom. This finding is in agreement with our previous suggestion [9] that such *d* functions are important in describing the bonding to second-row atoms when the valency of such atoms is increased from the natural value. Thus, in PF_3S, the formal excess valency of phosphorus is two whilst that of sulphur is zero. The change in phosphorus orbital populations on formation of the P–S bond, compared to the corresponding values for PF_3O [2] indicate that the degree of σ donation and π back bonding is less in PF_3S than PF_3O, reflecting the greater electronegativity of oxygen than that of sulphur.

In the calculations of PCl_3 and $POCl_3$, *d* orbitals were not included in the chlorine atom functions as, using the valency argument discussed above, they will not be important in discussing the P–Cl bonds. The phosphorus 3*d* population in PCl_3 though rather smaller than that in PF_3, is sufficiently large to indicate a significant excess valency on the phosphorus atom

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* The tabulated values for PF_3S in Tables 3—5 are for the calculation with unsplit *d* orbitals on both sulphur and phosphorus.

[9] I. H. Hillier and V. R. Saunders, *Chem. Comm.*, 1969, 1183.

resulting from π bonding with the chlorine atoms. The change in electron distribution on formation of PCl_3O from PCl_3 is very similar to the corresponding change calculated for PF_3O. The contributions to the P–O bond overlap populations are also very similar in both oxides. These findings suggest that the nature of the P–O bond in substituted phosphines is not critically dependent upon the nature of the phosphine. Indeed the calculated energies of the P–O bonds are very similar in both molecules being 60 kcal for PF_3O and 54 kcal for PCl_3O compared with the experimental values of 130 and 125 kcal [10] respectively.

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[10] National Bureau of Standards Technical Note 270—3, 1968.

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