Ab Initio Calculations of the Bonding in Phosphine, Phosphorus Trifluoride, and Trimethylphosphine

By I. H. HILLIER* and V. R. SAUNDERS
(*Chemistry Department, University of Manchester, Manchester,* M13 9PL)

Summary The bonding in the ligands PH_3, PF_3, and PMe_3 is described by *ab initio* SCF–MO calculations, and the results compared with experimental dipole moments and ionization potentials.

SPECULATION continues concerning the bonding of the ligands PH_3, PF_3, and PMe_3 to the transition metals.[1] An understanding of the bonding in these molecules is a prerequisite of a discussion of complex formation. For this reason we here report results of all-electron *ab initio* self-consistent-field molecular-orbital calculations of these molecules.

The basis orbitals consisted of a minimal set of Slater-type orbitals with best-atom exponents,[2] augmented by phosphorus 3*d* orbitals of exponent 1·4.[3] For computational ease, each member of this basis was expanded in a linear combination of three Gaussian-type functions, the expansion coefficients and orbital exponents being determined by a least-squares procedure.[4] To minimise the effect of the uncertainty in the 3*d* orbital exponent the ratio of the coefficient of the most diffuse to the other two Gaussian functions was determined by the self-consistent-field procedure.

The results are summarised in the Table. The occupancies of the phosphorus orbitals in these molecules obtained by a Mulliken analysis reveal definite trends.

There is a relatively large 3*d* population (0·7e) in PF_3, the majority (0·6e) being in the $3d_\pi(e)$ orbitals, and the 3*p* population decreases through the series PH_3, PMe_3, PF_3. The formal population of the phosphorus atom is in the order $PH_3 > PMe_3 > PF_3$. These formal charge distributions are reflected to some extent in the calculated dipole moments. These are in good agreement with the experimental values,[5] that for PF_3 showing the greatest discrepancy. The direction of the dipole in this molecule corresponds to $P^+–F^-$ and arises from the strong electron-accepting property of the fluorine atom (note large 2*p* population). The dipole moment for PH_3 ($P^-–H^+$) is mainly a one-centre (phosphorus) polarization effect. In the absence of 3*d* orbitals it is increased from 0·3D to 1·6D although the formal charge separation decreases. The moment of PMe_3, in the same direction as that of PH_3 in spite of the formal positive charge on the phosphorus, is strongly influenced by the polarity of the methyl groups, so that it is much less dependent than that of PH_3 on the inclusion of 3*d* orbitals in the calculation.

The nature of the P–X bonds is revealed by examination of the overlap populations shown in the Table, broken down into the individual σ and π components with respect to the P–X bonds.

Bonding in PH_3, PF_3, *and* PMe_3

Atomic populations

		PH_3	PF_3	PMe_3
Phosphorus	3*s*	1·64	1·51	1·55
	3*p*	3·48	1·89	2·98
	3*d*	0·26	0·71	0·19
Atomic charge		−0·32	0·95	0·35
X	1*s*	0·89	2·00	1·99
	2*s*		1·90	1·31
	2*p*		5·42	3·31
Atomic charge		0·11	−0·32	−0·61

Overlap populations

	Phosphorus orbital	X orbital	Overlap population
PH_3	3*s*	1*s*	0·08
	3*p*	1*s*	0·59
	3*d*	1*s*	0·11
PMe_3, PF_3*	3*s*	2*s*	−0·03 (−0·06)
	3*p*	2*s*	0·18 (0·04)
	3*d*	2*s*	0·02 (0·05)
	3*p*	$2p_\pi$	−0·02 (0·07)
	3*d*	$2p_\pi$	0·01 (0·19)
	3*s*	$2p_\sigma$	0·08 (−0·01)
	3*p*	$2p_\sigma$	0·40 (0·27)
	3*d*	$2p_\sigma$	0·06 (0·10)

* The values for PF_3 are given in parenthesis.

Highest filled and first virtual orbital

	Symmetry	Energy (ev)	Experimental ionization potential (ev)	Orbital form (%)						
				Phosphorus orbital			X orbital			
				3*s*	3*p*	3*d*	1*s*	2*s*	$2p_{x,y}$	$2p_z$
PH_3	3*e*	5·74			31	59	3			
	$5a_1$	−10·02	9·93	17	71		4			
PF_3	7*e*	4·14			59	30			1	3
	$8a_1$	−12·69	12·31	34	36	3			4	5
PMe_3	7*e*	6·58			30	53				3
	$8a_1$	−8·49	8·58	14	61	1			1	4

Dipole moment (D)

	Calculated	Experimental
PH_3	0·34	0·56
PF_3	1·44	1·03
PMe_3	1·08	1·19

In all three molecules there is appreciable σ-bonding involving the phosphorus 3*p* and 3*d*, hydrogen 1*s*, and carbon and fluorine 2*s* and 2*p* orbitals. In all three molecules the phosphorus 3*s* orbital contributes little to the bond population, the major contribution involving the phosphorus 3*p*, hydrogen 1*s*, and carbon and fluorine $2p_\sigma$ orbitals. In addition, in PF_3 there is significant π-bonding between the phosphorus 3*p* and 3*d*, and fluorine $2p_\pi$ orbitals, the major interaction being $3d_\pi$–$2p_\pi$. Such π-bonding is absent in PMe_3. Thus, the participation of phosphorus 3*d* orbitals in bonding may be correlated with the π donor ability of the group to which this atom is bonded, the methyl group being a very poor donor, and the fluorine atom a relatively good one, giving a significant $3d_\pi$ population.

A discussion of the donor and acceptor properties of these ligands requires the energy and form of the highest occupied and first virtual orbital. In all three molecules, the highest occupied orbital (a_1) is localized on the phosphorus atom, and is similar in form in both PH_3 and PMe_3, having 60—70% 3*p* character. In PF_3 this lone pair orbital has approximately equal (*ca.* 35%) 3*s* and 3*p* components with a little (*ca.* 3%) 3*d* character. There is excellent agreement between the values of the first ionization potential, calculated assuming Koopman's theorem, and the experimental values found from photo-electron spectroscopy.[6] The values for PH_3 and PF_3 are in line with the charges on the phosphorus atom; the lower value for PMe_3, in spite of the formal positive charge on the phosphorus, may be attributed to the large negative charge on the surrounding carbon atoms.

The first virtual orbital (*e*) is also localized on the phosphorus atom and is similar in form in both PH_3 and PMe_3, having phosphorus $3d$ and $3p$ components in the approximate ratio 2 : 1, this ratio being reversed in PF_3 The energy separation between the lone-pair orbital, and first empty *e*-orbital is approximately the same in all three molecules, PF_3 thus having the virtual orbital of lowest energy.

(*Received, January 28th*, 1970, *Com* 129)

---

[1] W A G Graham, *Inorg Chem* , 1968, **7**, 315

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

[3] D B Boyd and W N Lipscomb, *J Chem Phys* , 1968, **48**, 4968, 1967, **46**, 910

[4] W J Hehre, R F Stewart, and J A Pople, "Symposium of the Faraday Society," 1968, No 2, p 15, I H Hillier and V R Saunders, *Internat J Quantum Chem* , in the press

[5] A L McClellan, Tables of experimental dipole moments", Freeman, San Francisco, 1963

[6] J D Eland, J C Green, A F Orchard, and D W Turner, unpublished results