Electronic Structure and Inversion Barrier of Phosphine. An *Ab initio* SCF-LCAO-MO Study

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Summary Near-Hartree–Fock SCF-LCAO-MO calculations with geometry optimization on PH_3 reveal the electronic structure (*d* orbital participation, nature of the lone pair) and the barrier to phosphorus inversion.

THE electronic structure and molecular properties of tervalent phosphorus compounds have been subject to many experimental and theoretical investigations.[1] However only a few all-electron SCF calculations have been performed on the model compound PH_3,[2–4] and only one of them included a computation of the energy barrier to phosphorus inversion (25·4 kcal/mole).[2]

We report our results of a near-Hartree–Fock calculation of the PH_3 molecule. Calculations have been performed using the general program IBMOL[5] with a basis set[5] of twelve *s* and nine *p* gaussian functions on phosphorus and five *s*-functions on hydrogen (Sub-case SC 1); to these orbitals, two sets of *d* functions (exponents d_1 0·8 and d_2 0·2) on P and a set of *p* functions on H (exponent 0·3) have also been added (Sub-case SC 2).[†]

Calculations have initially been performed for several heights h of the PH_3 pyramid using the experimental P–H bond length;[6] the calculated optimal values $h = 0{\cdot}763$ Å and <H–P–H = 93° 50′ are thus obtained (experimental values:[6] $h = 0{\cdot}763$ Å; <H–P–H = 93° 50′). The r (P–H) bond length has then been optimized for <H–P–H = 93° 50′ and 120° (planar form). The calculated (SC 2) optimized geometry of the pyramidal form[‡] is found to be $h = 0{\cdot}763$ Å and r(P–H) = 1·4208 Å, as compared to experimental values[6] of 0·763 Å and 1·4206 ± 0·005 Å respectively. Such excellent agreement is not maintained when *d* and *p* polarization functions are not included (SC 1) (see Table).

The total energy (SC 2) amounts to −342·45595 a.u. which should be very near the Hartree–Foch limit (experimental total energy = − 343·42[2]), and is appreciably lower than previously reported values.[2–4]

d-Orbital participation in phosphorus compounds is a much debated question.[1] The Table clearly shows that the inclusion of *d*-orbitals (the presence of *p*-orbitals on H does not affect these conclusions as shown by calculations excluding *p* on H) leads to a noticeable improvement in energy and geometry. The total electron population in all twelve *d*-functions is quite small (0·19 e). The P–H bond is polarized in the P^+, H^- sense, in contrast with previous calculations.[2,3] The positive charge on P and the negative charge on H increase slightly in SC 2 as compared to SC 1, electron density being transferred from P to H. The inclusion of *d*-orbitals also shifts electron density into the P–H bonding region as seen from the increase in the P–H overlap population from SC 1 to SC 2 (Table).

In conclusion, *d*-orbitals on P (as well as *p* functions on H) participate to the bonding in the PH_3 molecule; they should be considered however as *polarization* functions,[7] increasing

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[†] The ternary axis of the molecule has been taken as the z-axis.

[‡] The energy of this form does not satisfy the mathematical criteria for a minimum in a function of two variables. However, as the experimental values are obtained for the variables in both cases, it seems very probable that the energy is at or very near to the true minimum.

the flexibility of the basis set and making new regions of space available to the electrons, and not as *d*-orbitals in the usual chemical sense.[7,8]§

Theoretical results for the PH_3 *molecule*

	Pyramidal form		Planar form	
	SC 1	SC 2	SC 1	SC 2
Total energy (a.u.)*	—342·4041	—342·4559	—342·3548	—342·3967
h Optimal‡ (Å)	0·721 (0·763)[6]	0·763 (0·763)[6]	—	—
H–P–H Angle optimal‡	97° 12′ (93°50′)[6]	93° 50′ (93° 50′)[6]	—	—
r(P–H) optimal‡ (Å)	1·4418 (1·4206)[6]	1·4208 (1·4206)[6]	1·4024	1·3852
Inversion Barrier* (kcal./mole) ..	30·9	37·2	—	—
Atomic populations[a]				
— P (3 *s*)	1·793 (0·336	1·566 (0·306)	1·514 (0·000)	1·181 (0·000)
— P (3 p_1)	1·550 (1·450)	1·510 (1·445)	2·003 (1·986)	1·918 (1·901)
— Total *d* on P	—	0·188 (0·002)	—	0·137 (0·000)
— Total *p* on H	—	0·025 (0·003)	—	0·068 (0·028)
— P (total)	14·955 (1·795)	14·927 (1·760)	15·200 (2·000)	14·934 (1·915)
— H (total)	1·015 (0·068)	1·024 (0·080)	0·933 (0·000)	1·022 (10·028)
P–H Bond overlap population[a] ..	0·333 (0·003)	0·389 (0·004)	0·348 (0·000)	0·427 (0·026)

* SC 1: *h* Optimal; *r*(P–H) experimental: SC 2: both *h* and *r*(P–H) optimized.

‡ SC 1: Optimal *h* and H–P–H angle for experimental *r*(P–H); Optimal *r*(P–H) for experimental H–P–H angle. SC 2: All parameters optimal. Experimental values are given in parentheses.

[a] Values in parentheses refer to populations in the lone.pair molecular orbital.

Hybridization theory predicts the phosphorus electronic lone pair to be nearly pure *s* character in view of the 93° 50′ H–P–H angle:[1] the dipole moment of PH_3 has been discussed in terms of zero lone-pair moment.[9] In contrast we find that the highest occupied molecular orbital, which is strongly localized on the P atom (88%) and represents the phosphorus lone pair, contains 15% P (3*s*) and 72% P (3*pz*) atomic orbitals (see electron population analysis in the Table). PH_3 thus possesses a highly directive lone pair, as does ammonia.

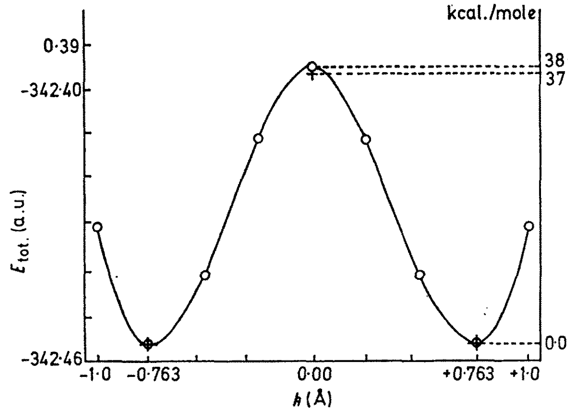

FIGURE. *Variation of the total energy* (SC 2) *of the* PH_3 *molecule as a function of the pyramid height* h *at constant* P–H (*experimental*) *bond length* (○). PH_3 *total energy including* P–H *bond l ength optimization* (+).

The barrier to phosphorus inversion is a theoretically and practically very interesting quantity. Whereas aliphatic tertiary amines undergo rapid inversion at the nitrogen site, optically active phosphines have been isolated indicating that the phosphorus inversion barrier is higher than *ca.* 25 kcal./mole.[1,10,11] The total energy variation during phosphorus inversion is shown in the Figure as a function of *h* [*r*(P–H) maintained at the experimental value]; a barrier of 38·2 kcal./mole is obtained. Optimization of both *h* and *r*(P–H) in the planar and in the pyramidal states leads to a phosphorus inversion barrier of 37·2 kcal./mole. The deletion of the polarization functions lowers the barrier to inversion by *ca.* 20%. It is also seen (Table) that the *d*-functions on P contribute more to the pyramidal than to the planar state, the reverse being true for the *p*-functions on the hydrogens.

We believe that the present value of the inversion barrier of PH_3 should be near to the real, still undetermined, value. Activation energies of 28—31 kcal./mole[11] have been obtained in tertiary phosphines such as R_2PPh (which should have a lower inversion barrier as in amines); a lower limit of *ca.* 35 kcal./mole may be estimated for a tertiary phosphetane from recently reported results.[12]

The results indicate also that the physical origin of the phosphorus inversion barrier as well as the characteristic changes accompanying the inversion process present many analogies with those for nitrogen inversion[13,14] [see for instance the $s \rightarrow p$ electron transfer (*ca.* 0·4 e; see Table) and the increase in overlap population]. The addition of polarization functions markedly affects the evolution of the various electronic energy terms as inversion proceeds; thus the extended basis set SC 2 is needed for a detailed description of the energetical origin of the PH_3 inversion barrier. However the qualitative origin of the barrier is not affected by the change in basis set.

The comparison of the theoretical pictures of phosphorus,

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§ A detailed discussion of the chemical meaning of *polarization* versus *participation* will be given in the final account of this work.

nitrogen,[13,15] carbanion,[14] and oxonium[14] inversion processes within the *ab initio* SCF–LCAO–MO framework leads to a general description of the physical origin of inversion barriers.

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