Theoret. Chim. Acta (Berl.) 41, 141–148 (1976)

A Configuration Interaction Study of Phosphine Using Bonded Functions

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Received July 28, 1975

A computational study is made of the effect of basis set upon the energy, properties and inversion barrier of the phosphine molecule. The calculations are performed at both the SCF and CI level. The flexibility of the double zeta basis is discussed in the light of the results.

Key word: Phosphine, CI study of ~

1. Introduction

A great deal of effort has, over the past few decades, gone into theoretical studies of the bonding and properties of phosphorus containing compounds. Phosphine, as the prototype of many organo-phosphines has been a special subject of study [1].

Although the latest calculations [2, 3] on PH_3 have given SCF energies said to be within 0.04 a.u. of the Hartree Fock limit, comparatively little attention has been paid to basis set effects on the energy, properties and inversion barrier. In this study, an attempt has been made to compare in these respects, the various basis sets available in the literature. The calculations were performed both at the SCF level and with limited CI. Since calculations with restricted basis sets only will be possible on the more complicated organic congeners or PH_3, the present study will have value in attempting to assess the validity of such calculations.

2. Description of the Basic Set

The available basis sets can be divided into three subgroups, viz.:

2.1. Fitted Minimal STO + d-Functions

The minimal Gaussian fitted STO basis set (FSTO) has the great advantage of having the fewest virtual MOs and this enables construction of a small CI expansion which may be easily analysed. This feature is particularly important in situations where the large number of electrons prevents construction of a full

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CI expansion. The major disadvantage of the basis set is the poor SCF energy it yields and the undue importance it may well accord to the *d*-functions in the bonding scheme. The basis set used in the calculations reported here was constructed from a linear combination of three GTOs [4] per STO exponent [5]. The *d* functions whose exponents [6] were taken as 1.22 were also fitted [7] by three GTOs.

2.2. Atomic Energy Optimised [4s, 3p]

This type of basis set gives the best atomic energy [8]. Also, the number of MOs is reasonably small and the CI expansion may be made fairly concise without imposing too many restrictions. The major disadvantage of this type of basis set is the lack of valence orbital flexibility. Two basis sets of this type [8a] were constructed. The basis AEO1 has a [1*s*] contraction on the hydrogen atoms [9] and the basis AEO2, a [2*s*] contraction. The scale factor for the hydrogen atom exponent was 1.275.

2.3. Molecular Double Zeta Accuracy [6s, 4p]

This is the most flexible basis set type and reasonably good SCF energies are expected. However, even for PH_3 this basis set gives many MO's and it is difficult to obtain a short CI expansion without making quite severe restrictions on the electron excitation pattern. Three examples of this type of basis set were studied. The DZO1 basis was abstracted from the literature [10]; a [1*s*] contraction (from five primitive GTOs) was used for the hydrogen atoms [9]. DZO2 was a recontraction of the DZO1 basis [11]; again a [1*s*] hydrogen atom contraction was used. DZO3 consisted of fewer primitive GTOs but the same number of CGTO [12]. The hydrogen contraction in this case was a [2*s*] expansion [12*b*].

The equilibrium (C_{3v}) molecular geometry of PH_3 has been taken from Ref. [11] and the bond length in the planar (D_3h) geometry has also been taken as the equilibrium bond length (2.680 a.u.).

3. Calculations

3.1. Energy of the Equilibrium Configuration

The Rootham-Hall SCF results were evaluated using a double precision version of Polyatom II [13] and are shown in Table 1. The effects of a polarizing set of GTO *d*-functions were also calculated (except on the FSTO+*d* basis). The *d*-orbital exponent was taken to be 0.6, this value having been found (from an optimisation study [14]) to be most suitable for all the basis sets studied.

Table 1 shows the total energies obtained. The difference between the minimal STO basis and the extended bases can be seen to be considerable. The difference between DZO1 and DZO2 has already been discussed [11] with reference to HC2 and will not be elaborated here. The basis AEO2 gives an energy 0.012 a.u. above the best literature result [11].

Table 1. SCF energies

Basis Set	Total Number of Functions	E_{SCF} (a.u.)	ΔE_{SCF} (*sp*–*spd*)
FSTO + *d*	18	−338.7985	–
AEO1	22	−342.4419	0.0563
AEO2	25	−342.4484	0.0512
DZO1	27	−342.2275	0.0537
DZO2	27	−342.4360	0.0524
DZO3	30	−342.3568	0.0492
Ref. [11]	39	−342.4603	–

The method of performing the CI calculations has been described fully elsewhere [14, 15] and it may be summarised as follows:

(1) The AO integrals are transformed [16] to their MO counterparts.
(2) The Bonded Function [17] (BF) expansion consisting of single and double excitations was constructed. Only five types of excitations were permitted[1]. These may be symbolised as:

A (single excitations) $a^2 \longrightarrow ar$
B (identical pair replacements) $a^2 \longrightarrow r^2$
C (non-identical replacements) $a^2 \longrightarrow rs$

$$\left.\begin{array}{l}\mathrm{D}\\ \\ \mathrm{E}\end{array}\right\}\text{(interpair replacements)}\quad a^2b^2 \begin{array}{l}\nearrow\; ar\ bs\\ \\ \searrow\; as\ br\end{array}$$

(3) The upper triangle of the CI Hamiltonian matrix was constructed by the Direct method [14, 15].
(4) The CI energy and coefficients were evaluated by the Nesbet method [18].
(5) A set of approximate natural orbitals are formed from the one-particle spinless density matrix constructed using the CI vector coefficients.

The ground state symmetry adopted MO sequence in PH_3 is[2]

$$1a_1,\ 2a_1,\ 1e_x,\ 1e_y,\ 3a_1,\ 4a_1,\ 2e_x,\ 2e_y,\ 5\mathrm{a}_1.$$

The full BF expansion for the AEO2 *spd* basis consists of nearly 17,300 BF (including those disappearing due to symmetry constraints). However, the lowest lying 5 MOs are almost completely localised in phosphorus [19] and are treated as an invariant core in the CI calculation. A series of calculations were performed using the AEO2 *spd* basis set. The various expansion lengths were obtained by imposing restrictions on the number of virtual MO's participating in the excitation process. Table 2 gives the expansion lengths and energies for these calculations. It can be seen that the calculation CI3 yielded an energy below the best literature result [20], but the electronic correlation energy recovered is probably only a small percentage of the total.

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[1] The orbitals *a*, *b* are occupied and *r*, *s* virtual, in the molecular SCF ground state.

[2] According to the C_{3v} point group. The sequence is ordered by increasing MO energy.

Table 2. CI Calculations using the AEO2 *spd* basis set

Calculation	Expansion Length	E_{CI} (a.u.)	$E_{CI} - E_{SCF}$[a] (a.u.)	$E_{CI} - E_{HF}$[b] (a.u.)
CI1	179	−342.5037	−0.0552	−0.0037
CI2	250	−342.5086	−0.0602	−0.0086
CI3	304	−342.5116	−0.0631	−0.0116

[a] $E_{SCF} = -342.4484$ a.u.

[b] $E_{HF} = -342.45$ a.u. (estimated by Ref. [20]). The entries in this column are the amounts of valence electron correlation energy recovered.

3.2. *Dipole Moment*

The dipole moment of PH_3 was evaluated using the basis sets presented in Section 2. In order to make a comparative study of the basis sets, the property was evaluated at the SCF and CI level using both the *sp* and *spd* basis sets. The results are shown in Table 3. The CI calculations were performed using the single and identical pair replacement BF (types A and B). Approximate Natural Orbitals were used to calculate the CI dipole moments. The effects of CI on dipole moments have been studied by Green [22] and Mulliken [23] and their conclusions are borne out by these results. The results show that CI reduces the dipole moment result by a small amount (0.02 to 0.05D) for the *sp* bases. However, in the *spd* bases, the reverse trend is observed. The *sp* bases show μ_{CI} lower than μ_{SCF}. CI is causing a flow of electron density into the P–H bond region, compensating for the rather poor hydrogen atom description. Similarly, the *d* functions decrease the charge density close to Phosphorus; the CI effect is therefore to reverse this trend and

Table 3. Dipole moments[a]

Basis Set	μ_{CI}[d] (Debye)	μ_{SCF} (Debye)	Difference (CI–SCF)
FSTO+*d*	0.219		
AEO1 *spd*[b]	1.577	1.551	0.026
sp	(2.160)[c]	(2.200)	−0.040
AEO2	1.250	1.247	0.003
	(1.678)	(1.724)	−0.046
DZO1	0.438	0.389	0.049
	(0.937)	(0.903)	0.034
DZO2	1.565	1.529	0.036
	(2.120)	(2.139)	−0.020
DZO3	0.767	0.759	0.008
	(1.160)	(1.183)	−0.023
Ref. [19]	–	1.172	–
Ref. [11]	–	0.838	–
Ref. [20]	1.247	1.276	−0.030
	–	(1.716)	–

[a] Experimental result is 0.578D from Ref. [21].

[b] The *d* function exponent was 0.60 in each case.

[c] The *sp* basis result is shown in parentheses.

[d] A positive result signifies polarisation P^{-}–H^{+}.

restore balance. That the dipole moment result is very sensitive to basis set is evident from the large spread of results in Table 3. It has also been found that the dipole moment result is sensitive to the nature of the CI expansion. Using the basis set AEO2, the CI calculation using the BF types *A*, *B* and *C* was performed. The resulting approximate NOs gave a dipole moment of 1.690D, considerably closer to the SCF result than the expansion using the single and identical pair replacements alone. These results can be explained qualitatively in terms of the contribution made to the CI wave function by each BF type. (An exploratory study of HF from this viewpoint is in preparation for publication.)

3.3. Inversion Barrier

The inversion barrier of NH_3 has received very close attention [20, 24]; PH_3 however, has not had similar treatment. In this study, no attempt has been made to optimise the geometry of either the pyramidal or planar conformers of PH_3.

The SCF energies for both structures were evaluated using the basis sets described in Section 2. A small CI calculation using the full set of single excitations (*A* type BF in Section *3.1*) and identical pair replacements (*B* type BF) was performed using the MOs from the SCF calculations as an initial guess to the approximate NOs. The inversion barrier (E_{planar}-E_{pyramid}) was then evaluated at the SCF and CI level of accuracy. Tables 4 and 5 show the SCF and CI results respectively.

From the SCF calculations on each of the basis sets, it can be seen that addition of a set of *d* functions onto the central atom increases the barrier height by approximately 0.5 eV. This behaviour can be directly attributed to the nature of the *d* functions. In the pyramidal structure, the d_{xz} and d_{yz} orbitals contribute to bonding MOs; in the planar conformer, these orbitals are perpendicular to the molecular plane and play no part in the bonding scheme. The *d* functions therefore have an adverse effect on the inversion barrier because of the unbalanced participation

Table 4. SCF barrier heights

Basis[a] Set	E_{pyramid}[b] (a.u.)	E_{planar}[c] (a.u.)	Barrier[d] (eV)
FSTO+*d*	−338.7986	−338.7178	2.19
AEO1 *sp*	−342.3856	−342.3482	1.01
spd	−342.4419	−342.3929	1.60
AEO2 *sp*	−342.3972	−342.3486	1.32
spd	−342.4484	−342.3830	1.78
DZO1 *sp*	−342.1738	−342.0638	2.98
spd	−342.2275	−342.0978	3.52
DZO2 *sp*	−342.3871	−342.3507	0.99
spd	−342.4395	−342.3846	1.49
DZO3 *sp*	−342.3076	−342.2558	1.41
spd	−342.3568	−342.2880	1.87

[a] The *d* function exponent was 0.6 in each CGTO basis set.
[b] Nuclear repulsion energy = 17.5603 a.u.
[c] Nuclear repulsion energy = 17.4373 a.u.
[d] Experimental value of inversion barrier is between 1.2 and 1.4 eV.

Table 5. CI barrier heights

Basis Set	E_{pyramid} (a.u.)	E_{planar} (a.u.)	Barrier (eV)
FSTO + *d*	−338.8328	−338.7630	1.89
AEO1 *sp*	−342.4343	−342.3934	1.11
spd	−342.4964	−342.4390	1.56
AEO2 *sp*	−342.4451	−342.3933	1.40
spd	−342.5020	−342.4378	1.74
DZO1 *sp*	−342.2278	−342.1184	2.97
spd	−342.2869	−342.1673	3.24
DZO2 *sp*	−342.4273	−342.3912	0.98
spd	−342.4805	−342.4322	1.31
DZO3 *sp*	−342.3572	−342.3046	1.43
spd	−342.4140	−342.3400	1.76

in the conformers. This effect has been noticed previously [3] in PH_3 and also in NH_3, by Kari [25].

Comparison of the AEO1 and AEO2 bases shows the effect of variation of the s function expansion on the hydrogen atoms (since both basis sets have the same phosphorus atom description). AEO2 basis gives a barrier height 0.3 eV greater than AEO1. This result may be rationalised, qualitatively, in terms of the overlap between the phosphorus p orbitals and the hydrogen s functions. The p-s bonding may be thought of as three components: p_x-s, p_y-s and p_z-s. Since the AEO2 basis has a larger s expansion than AEO1, it may be assumed that the p_z-s bonding is stronger in the former basis. Consequently, in the planar structure, the loss of this bonding gives a higher molecular energy and thus an increased barrier height. Thus, as the number of hydrogen functions is increased the barrier increases. This effect is probably the cause of the difference in the results for DZO2 and DZO3 (since the number of functions on phosphorus is the same; however, the number of functions on the hydrogen atoms is greater in the latter basis set).

The large barrier predicted by the FSTO + d basis can be rationalised simply by examining the importance of the d functions. Since the *sp* basis is minimal, the d functions behave as valence p functions and therefore the loss of the d_{xz} and d_{yz} orbitals has a marked effect on the energy of the planar structure.

It can be seen from Table 5 that the CI result for the barrier height using the *spd* basis is always lower than the corresponding SCF result. In the *sp* basis sets, the reverse trend is noticed (the DZO1 and DZO2 show a small decrease in barrier height however).

In the *spd* bases, the lower barrier height is due to the involvement of the d_{xz} and d_{yz} orbitals in the bonding in *both* the planar and pyramidal structure. Therefore, the destabilising effect of addition of a set of d functions is reduced. The *sp* results can be rationalised using an argument based on the electron distribution variation caused by the effects of CI. The pyramidal P–H bond density is being enhanced by the CI effects. However, in the planar structure, a lower charge is observed. Thus, the barrier is increased.

The AEO1 and DZO3 *sp* bases give a result closest to experiment. However, it is useful to consider the accuracy of these results compared to that obtained simply by variation of the central atom *d* function exponents.

Calculations with the AEO2 basis show that a maximum barrier height is obtained (1.84 eV) coinciding with the value of the exponent which gives the optimum energy of the pyramidal structure.

4. Summary and Conclusions

The CI results have shown that despite examining a cross section of the available basis sets, the total energy is very poor. On average, only 0.05 a.u. has been recovered by a BF expansion of between 80 and 200 terms. Despite also giving the lowest CI energy for PH_3, an expansion of 300 BF gave a result only 0.065 a.u. below the SCF result. Therefore the inadequacy of these bases is apparent. In the dipole moment study and inversion barrier calculations, the susceptibility of the result to variation in basis set is also evident. It is therefore concluded that before any quantitative investigations of the behaviour of these second row hydrides may be attempted, it will be necessary to derive basis sets of considerably greater flexibility than double zeta accuracy.

Acknowledgements. We would like to thank the SRC and the SRC Atlas Computer Laboratory for a generous allowance of time on the IBM 360/195; also to thank Dr. G. H. F. Diercksen for allowing us to use his four index transformation programme. Thanks are also due to the Carnegie Trust for a grant to JMS.

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