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An SCF Study of P_4O_6 and P_4O_{10}

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The electronic structures of the oxides P_4O_6 and P_4O_{10} are calculated by the self-consistent molecular orbital method including all valence electrons and the 3*d* orbitals on phosphorus. It is found that the former molecule appears to be virtually non-polar whilst in the latter, the P—O (terminal) bonds are highly polar. The bond order matrix shows that the internal P—P bonding in the P_4 unit is not marked.

Introduction

An interesting feature of molecules which contain second-row atoms is the extent to which the formally empty 3*d* orbitals participate in the bonding scheme. This problem is particularly cogent in the case of phosphorus compounds and in order to throw light on the area, a number of *ab initio* calculations have been performed [3, 4, 8].

The *ab initio* approach, however, becomes computationally infeasible for large molecules because of the size of basis set required for accuracy: in this respect *minimum* basis set *ab initio* calculations may well be less accurate than semi-empirical ones. This point has yet to be fully investigated.

In the present paper a rationale of the bonding in the phosphorus oxides P_4O_6 and P_4O_{10} is attempted in terms of the LCAO SCF CNDO formalism [6, 9]. The calculational scheme employed was essentially similar to that of our previous calculations on phosphorus compounds [1].

As stated above, because of the size and complexity of *ab initio* calculations, it is clear that semi-empirical treatments of molecules of chemical interest will be required for some time to come. However, it is important that comparisons between *ab initio* and CNDO type calculations be made for molecules containing second-row atoms in order to establish the degree of reliability of the latter method. Hence, we carried out calculations on phosphine and phosphine oxide, both of which have been studied using Gaussian-type orbitals [3, 4, 8]. All the details of these calculations are to be found in Ref. [1b]. For P_4O_6 and P_4O_{10}, bond distances and angles were abstracted from standard compilations [5]. Burns' orbitals were chosen as the basis set and, for the 3*d* group, an exponent corresponding to a "diffuse" orbital was employed: this choice was made in order that our calculated results would be directly comparable to those for the P_4 tetrahedron [1]. This is important, since both P_4O_6 and P_4O_{10} are based structurally on the P_4 tetrahedron. In any case, diffuse *d* orbitals should be more appropriate, since in P_4 itself their radial extension is such that they are able to overlap with orbitals defined in the opposite faces of the tetrahedron [1]. All calculations were performed on the Strathclyde University ICL 1905 computer, using a symmetry based SCF programme.

Results and Discussion

An abstract of the principal results for PH_3 and PH_3O is given in Table 1 together with data from the *ab initio* calculations. No detailed discussion need be given here but it is at once clear that, for these two systems, our results are in substantial agreement with those of the more sophisticated treatments. This result encourages the belief that a CNDO-based method can be a reliable tool for calculating valence electronic structures for phosphorus compounds.

The results of the calculations on P_4O_6 and P_4O_{10} are now discussed under three heads

Table 1. *Calculated data for phosphine and phosphine oxide*

Atomic populations	PH_3				PH_3O		
	Present work[f]	Previous work			Present work[f]	Previous work	
		[a]	[b]	[c]		[d]	[e]
P 3*s*	1.57	1.64	1.566	1.54	1.51	1.20	—
3*p*	3.27	3.48	3.173	3.23	2.76	2.36	—
3*d*	0.14	0.26	0.188	0.09	0.37	0.36	—
Nett charge on P	+0.02	−0.32	+0.073	+0.14	+0.36	+1.08	+0.245
Nett charge on H	−0.00	+0.11	−0.024	−0.04	−0.01	−0.12	+0.250
O 2*s*	—	—	—	—	1.61	1.84	—
2*p*	—	—	—	—	4.71	4.84	—
Nett charge on O	—	—	—	—	−0.32	−0.72	−0.334
Energy of highest bonding orbital (eV)	−11.7	−10.02	—	—	−10.6	—	−10.3

[a] Ref. [4].
[b] Lehn, J. M., Munsch, B.: Chem. Comm. **1970**, 1321.
[c] Ref. [8].
[d] Ref. [3].
[e] Ref. [8]; the data in this paper are not analysed as separate *s*, *p*, and *d* orbital populations.
[f] "contracted" *d* orbitals were included on phosphorus (see Ref. [1b]).

a) Charge Distribution

A population analysis performed on the molecules with and without inclusion of 3*d* orbitals in the basis set yielded the charge distribution over the atomic skeleton shown in Fig. 1. The axis system illustrated here determines the orientations of the orbitals on all the atoms. First of all, the results show clearly that 3*d* orbital participation in phosphorus bonding is influential and that one of the effects of this participation is to even out the relative charges on the phosphorus and oxygen atoms and so to make the electronic picture more realistic. This seems to be a general effect in P–O compounds [1, 7]. The actual extent of the *d*

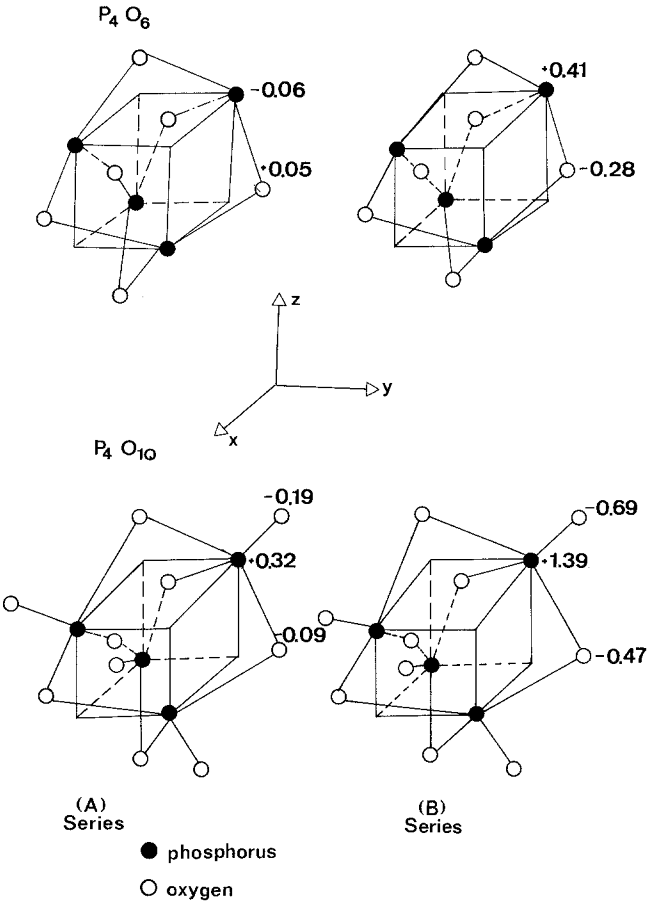


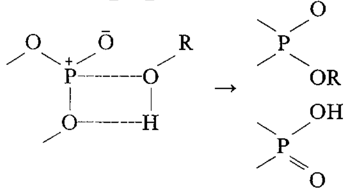
Fig. 1. Charge distribution in P_4O_6 and P_6O_{10}. Series A; 3*d* orbitals included; Series B; 3*d* orbitals neglected

Table 2. *Orbital occupation in* P_4O_6 *and* P_4O_{10}

	P_4O_6		P_4O_{10}	
	Without *d* orbitals	With *d* orbitals	Without *d* orbitals	With *d* orbitals
P 3*s*	1.273	1.046	0.951	0.780
3*p*	3.312	2.745	2.660	2.225
3*d*	—	1.275	—	1.672
Nett charge on P	+0.415	−0.066	+1.389	+0.323
O (bridge) 2*s*	1.113	1.089	1.155	1.102
2*p*	5.163	4.866	5.311	4.995
Nett charge on O (bridge)	−0.276	+0.045	−0.466	−0.097
O (term) 2*s*	—	—	1.232	1.230
2*p*	—	—	5.458	4.955
Nett charge on O (term)	—	—	−0.690	−0.185

orbital participation is reflected in the calculated orbital charge densities (Table 1) and is seen to be substantial. It is striking that the *d* orbital population is so large and, moreover, it is noteworthy that the *d* electron density increases with the greater number of oxygens in the molecule, i. e., it is greater in P_4O_{10} than in P_4O_6. This, however, is consistent with early ideas on the mode of *d* orbital participation [2], in which it was suggested that electronegative groups around phosphorus would help contract the 3*d* orbitals and mix them in to a greater extent.

In P_4O_6 the charge distribution over the PO_3 units is very similar to that in the hypothetical trihydroxyphosphine [1] an isomer of phosphorous acid; thus, P_4O_6 appears to be virtually electronically neutral. The polarity and multiplicity of the P–O bond in these oxides and, indeed, in P–O compounds in general, is a matter of some importance, since these are the properties which can help rationalise the chemical behaviour of the compounds. It is of considerable significance that the charge separation across the P–O (terminal) bond in P_4O_{10} is marked even after attenuation by the 3*d* orbitals. An examination of the results for other P–O compounds or ions which have been studied (the phosphate series [7], Me_3PO, PH_3O [1, 3, 8]) reveals that the degree of charge separation in P_4O_{10} is only matched by that of the P–O bond in PH_3O. It is significant that the latter compound has not yet been prepared, possibly for this very reason; it would lead to great lability. The high reactivity of P_4O_{10}, especially its avidity for polar hydroxy compounds, is hardly surprising in view of this highly polar charge distribution. This finding is consistent with the supposed mode of reaction of P_4O_{10} with alcohols and water [10], i. e.,



The interesting point here is that the reaction mechanism depends on the attachment of the acidic hydrogen atom to a bridging oxygen which is the *least* negative of the two types. This may reflect the relationship of the electronic properties of the P_4 unit in the oxides to that of P_4 itself, since the edges and faces of the latter basic unit are regions in which charge density is highly concentrated [1].

b) Bond Orders

Because of the relationship of both molecules to the P_4 tetrahedron, it is first of interest to examine the changes brought about in the bonding of the latter by addition of oxygens at corners and along edges of this unit. In P_4 the stability of the molecule is enhanced by strong $3p_\pi 3p_\pi$ bonding along the tetrahedron edges, accompanied by 3-centre φ bonding on the trigonal faces; the latter is strengthened by interaction with 3*d* orbitals centred on corresponding atoms, i. e., opposite the faces.

When we pass to P_4O_6 and P_4O_{10} the essential P_4 unit is retained, although it is somewhat enlarged in these systems, the P–P distance increasing from 0.221 *nm* to nearly 0.3 *nm* [5]. In forming P_4O_6 from P_4 the edge oxygen atoms appear to add across the edge $p_\pi p_\pi$ bonds of P_4 and so weaken them. This means that the expansion of the tetrahedron is energetically favoured, since repulsive forces will assume more importance when bonding is diminished. Moreover, in P_4O_{10}, involvement of the phosphorus orbitals in bonding to the external oxygens will remove electron density from inside the tetrahedron where it appears to be concentrated in P_4. This will decrease the nuclear shielding between the four phosphorus atoms and this, in turn, can be relieved by cage expansion. The bond orders calculated bear out this interpretation: the $p_\pi p_\pi$ edge bonds of P_4 are virtually nonexistent in the oxides whilst the *d* orbitals cease to interact markedly with the opposite face orbitals: P–P bond orders in general are much reduced.

The P_4 tetrahedron with P–P = 0.221 *nm* could, in principle, be retained with narrow $P\widehat{O}P$ bridging bond angles: (they would have to be $\sim 86^0$). Obviously, nuclear repulsion between oxygens would be increased in this situation and it seems that this factor militates against the retention of the small P_4 unit, especially as it must lose P–P edge bonding through linking to oxygen.

The P–O (terminal) bonds are multiple in nature and have a considerable π component resolved from the *p* and *d* orbitals on phosphorus. This is consistent with the observed shortness of this bond in P_4O_{10} (1.39 Å [5]).

c) Energies

Both systems retain full tetrahedral symmetry and so the eigenvalues fall into both doubly and triply degenerate sets. In P_4O_6 the highest bonding and lowest antibonding orbitals are of *t* and *e* symmetry respectively and have energies −6.6 and 9.3 eV. In P_4O_{10} the corresponding energy levels are *t* and *a*, with energies −9.7 and 11.2 eV.

With regard to the total energies the *d* orbitals lower the energy of P_4O_6 by 6.6 % and of P_4O_{10} by 6.0 %. This is rather less than that calculated for P_4 (11 %).

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