Photoelectron Spectral Assignments Based on *Ab Initio* MO Calculations for the Bicyclic Phosphorus Compounds $P[OCH_2]_3CMe$ and $P[CH_2O]_3CMe$

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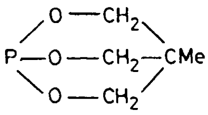
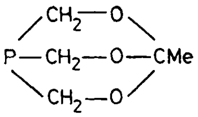
Summary *Ab initio* MO calculations on the title compounds are in good agreement with the recently published photoelectron spectra but not with the corresponding proposed MO scheme; the calculations show the first PE band to be mainly phosphorous in character rather than oxygen.


(I)


(II)

Recently, Cowley, *et al.*[1] reported the photoelectron (PE) spectra of a variety of phosphines and phosphites. A valid assignment of the spectra of the bicyclic phosphites (I) and (II) was a key component in their simplified MO model. They assigned the first ionization potential (IP) to oxygen lone pairs, while the phosphorous lone pair was assigned to a band at higher IP. This assignment is contrary to what one would expect based on the electronegativity. We felt that this question could best be resolved by rigorous Hartree–Fock–Roothaan MO calculations.[2]

Table 1. Geometric data for $P(X–Y)_3C–Me$.

Compound	X	Y	Bond lengths Å P–X	X–Y	Y–C	Bond angles/° XPX′	PXY	XYC	YCY′	YCMe
(I)	O	$C(H_2)$	1·61	1·45	1·52	100·10	117·50	111·05	108·50	110·85
(II)	$C(H_2)$	O	1·83	1·45	1·45	98·90	110·50	113·54	113·27	105·34

The basis functions were best atom exponents[3] expanded into three Gaussian functions.[4] A phosphorus 3*d* function with an exponent equal to that of the 3*p* function was included in the basis set. Calculations of similar quality have shown satisfactory agreement with the PE spectra of other similar phosphorus compounds.[5] The geometries of these molecules were based on the averaged values of equivalent bond lengths and angles obtained from *X*-ray crystallographic data. The values for (I) were those for $P[OCH_2]_3C–CH_2Br$[6] while the average values for both phosphine- and phosphite-co-ordinated $P[OCH_2]_3P$[7] were used for (II) with the substitution of C–Me at the phosphite bridgehead. The C–H bond lengths and angles in methanol[8] were used for the CH_2 and Me groups. The key geometrical parameters are listed in Table 1. Table 2 contains the experimental IPs, the MO assignments of Cowley, *et al.*,[1] the calculated IPs based on Koopmans' theorem[9] and our assignments.

Table 2. PE band assignments in eV.

Compound	Exptl. IP	Ref. 1	Calc. IP	This work
(I)	9·95	a_2(O)	9·2	a_1(P)
	10·43	*e*(O)	10·0	a_2(O)
	10·6	a_1(P)	10·3	*e*(O)
(II)	9·14	a_2(O)	8·8	a_1(P)
	9·97	*e*(O)	9·6	*e*(O)
	10·34	a_1(P)	10·3	a_2(O)

The major difference is that we assign the P(a_1) orbital as the lowest energy PE band, whereas this orbital is assigned the highest energy band by Cowley, *et al.* Their MO scheme depends upon placing the atomic orbitals of P lower in energy than those of O. The relative values of the diagonal energies in the self-consistent field matrix are determined largely by the relative electronegativities. Thus, the predominantly P orbitals would have a higher diagonal term than those of O, which would result in the P(a_1) being the first ionization. This conclusion is confirmed by our *ab initio* calculations, and we believe that the assignments of Cowley, *et al.* are incorrect.

The calculations also suggest that the relative positions of the oxygen lone pair in (I) are $a_2 < e$ but are reversed in (II). A substantial interaction between the O(*e*) orbitals and the *e* set of the P(*d*) system is predicted by the calculation for (I), which is, of course, absent in (II). This O(2*p*)–P(3*d*) interaction is in part responsible for lowering the *e* orbitals below the a_2 in the phosphite (I).

Additional support for our assignments is seen in the relative peak intensities in the spectra. The PE bands of non-bonding electrons tend to rise sharply on the low energy side and trail off more slowly on the high energy side owing to the overlap of the vibrational structure. Because of this characteristic shape, the large overlap of the P(a_1) band with O(a_2) makes the a_2 and *e* bands of (I) (Figure 8 in ref. 1) seem of approximately equal intensity.

Although the calculated IP's do not agree exactly with the experimental values, because of the limitations of Koopmans' theorem and the near minimal basis set employed, there is a very good qualitative agreement. We do not believe that calculations with larger basis sets or those which avoid the use of Koopmans' theorem would change our conclusions. In light of these calculations and arguments we conclude that our new assignments are correct and that, in similar compounds containing P and O, the IP of the P lone pair will be less than those of the O lone pairs. This conclusion is also supported by some recent work on the PE spectra of other phosphorous ligands co-ordinated to transition metal carbonyls.[10]

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