MOLECULAR PHOTOELECTRON SPECTROSCOPIC STUDIES OF BONDING AND STEREOCHEMICAL PROBLEMS IN PHOSPHORUS CHEMISTRY

Alan H. Cowley[a]

[a] Department of Chemistry, The University of Texas at Austin, Austin, Texas, USA

PLEASE SCROLL DOWN FOR ARTICLE

MOLECULAR PHOTOELECTRON SPECTROSCOPIC STUDIES OF BONDING AND STEREOCHEMICAL PROBLEMS IN PHOSPHORUS CHEMISTRY †

ALAN H. COWLEY

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712 USA

(Dedicated in memoriam to Jeremy I. Musher who made many contributions to the theory of bonding in phosphorus compounds.)

This article is concerned with the application of the relatively new technique of molecular photoelectron spectroscopy (pes)[1,2] to some bonding and stereochemical problems in phosphorus chemistry. No attempt will be made to infer that pes is a *deus ex machina* capable of functioning as the final arbiter on all controversial bonding problems; rather the general tenor will be one of unbiased examination of a selection of currently unresolved questions with a recently developed tool. In essence the pes method involves the measurement of the various first ionization potentials (IP_X) of a neutral molecule in the vapor phase. In the photoionization process the molecule M is ionized to its radical cation M^+ by means of a photon of energy $h\nu$,

$$M + h\nu \rightarrow M^+ + e^- \quad . \tag{1}$$
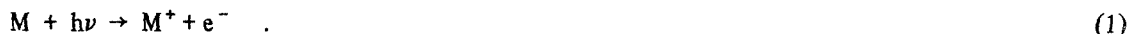
From the standpoint of the conservation of energy the photon energy which is not utilized for the ionization process must be emitted as the kinetic energy of the ejected electron (E_k),

$$h\nu = IP_X + E_k \quad . \tag{2}$$

Most pes spectrometers employ He(I) photons of energy 21.21 eV for the photoionization process[2,3] hence the various first ionization potentials up to 21.21 eV are readily derived by measurement of the kinetic energies of the emitted electrons,

$$IP_X = 21.21 \text{ eV} - E_k \quad . \tag{3}$$

The resulting plot of ionization potential *versus* intensity in counts per second is referred to as a photoelectron spectrum. The ionization potentials, IP_X, represent the differences in energy between the ground state of the molecule and its (several) radical cation states. Providing that for example no gross geometrical changes accompany the photoionization process, it is customary to employ Koopman's theorem[4] to relate the various ionization potentials to the appropriate orbital energies (ϵ_1),

$$\epsilon_i = -IP_X \quad . \tag{4}$$

In a crude sense a photoelectron spectrum can be regarded as a horizontal mapping of molecular orbital (MO) energies.

Two features will prove to be of value in regard to spectral assignment. Consider first the presence or absence of vibrational fine structure. In the case of a strongly bonding (Figure 1a) or strongly antibonding (Figure 1b) MO the internal coordinates *r* change markedly in proceeding from the ground state (M) to the radical cation state (M^+). Consequently the Frank-Condon principle requires that several vibrational transitions will accompany the ionization process and vibrational fine structure will be apparent in the pes. On the other hand there is little difference in internal coordinates of M and M^+ in the case of a non-bonding or weakly bonding MO (Figure 1c) and as a result no vibrational fine structure will be discernible. So called "lone pairs" of electrons fall in this latter category. The second spectral feature is pes peak intensity. Photoionization cross sections are dependent *inter alia* on the symmetry and orbital character of the MO from which the electron is removed[5] and the relative energies of the light source and the MO in question. However, it is generally found that there is a relationship between the orbital degeneracies and photoionization cross sections

---

† Plenary Lecture. The Vth International Conference of Organic Phosphorus Chemistry, Gdansk, Poland, September 1974.

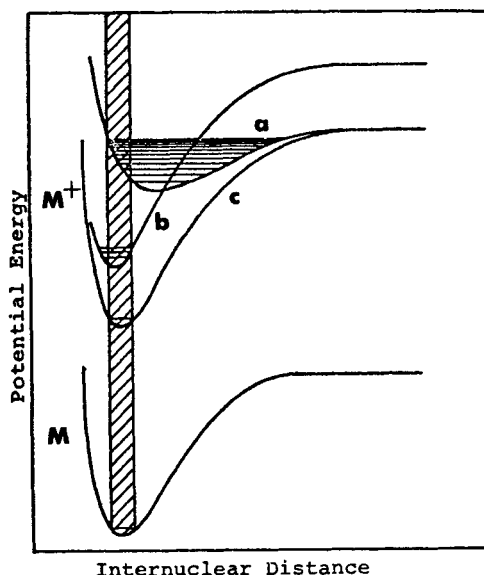in the sense that the pes intensities are in the order triple > double > single.

FIGURE 1   The Franck-Condon principle.

The foregoing principles can be illustrated by considering first the pes of phosphorus pentafluoride,[6] a molecule which plays an important role in phosphorus chemistry for both stereochemical dn theoretical reasons. In fact, several semi-empirical MO calculations[7-11] and one *ab initio* MO study[12] (Table I) have been carried out on this interesting molecule. However, it is readily apparent that there is a generally poor agreement between these calculations not only with respect to the sequencing of the MOs but also in regard to the magnitudes of the eigenvalues. The determination of the pes of PF_5 therefore seemed appropriate. Taking the molecular geometry of PF_5 to be D_{3h}[13] and assuming that the fluorine $2s$ orbitals will be of too low energy to be detectable by He(I), pes simple group theoretical considerations lead to a prediction of ten MOs (Table II), six of which are non-bonding combinations of π-type symmetry, the remaining four being $P\text{-}F(2p)$ σ bonds. Assuming that there is no sigma-pi mixing one expects that in general the π-type non-bonding combinations will be of higher energy (i.e. less stable) than the P-F σ-bonding MOs, a view which is borne out by the molecular orbital calculations (Table I).

TABLE I

Computed molecular orbital energies (eV) and experimental first ionization potentials[a] (eV) for phosphorus pentafluoride

BTBJ[b] $s/p/5d$[c]	VESCF[d] s/p	VESCF[d] $s/p/d$	VESCF[d] $s/p/3d$	NISEMO[e] s/p	ARCANA[e] $s/p/5d$	Ab initio[f,g] No d functions	Ab initio[f,g] with d functions	Experimental	Assignment
$-15.87e'$	$-16.92a'_1$	$-18.80a'_1$	$-19.10a'_1$	$-16.57a''_2$	$-14.94e''$	$-18.53e''$	$-18.09e''$	15.54	e' or e''
$-16.65a'_1$	$-24.85a''_2$	$-25.21e'$	$-25.42a''_2$	$-16.64a'_1$	$-15.30e'$	$-18.67a'_1$	$-18.61e'$	16.46	e' or e''
$-16.87e''$	$-24.98e'$	$-25.31a''_2$	$-25.56e'$	$-16.54e''$	$-15.90a'_1$	$-19.10e'$	$-18.91a''_2$	16.75	a''_2
$-17.22a''_2$	$-34.53a'_1$	$-35.10a'_1$	$-35.27a'_1$	$-17.16e'$	$-16.00a''_2$	$-19.42a''_2$	$-19.29a'_1$	17.13	a'_2
$-18.17a'_2$				$-17.60a'_2$	$-18.42a'_2$	$-20.22a'_2$	$-19.64a'_2$	17.79	a'_1
$-18.32a'$				$-17.85e'$	$-19.12e'$	$-20.82e'$	$-20.76e'$	18.43	a'_1 or a''_2
$-20.55e''$				$-19.37e''$	$-19.24e''$	$-21.96e''$	$-21.88e''$		

$-20.61a''_2$	$-19.40e'$ $-20.20a''_2$	$-23.67a''_2$	$-23.18a''_2$
$-21.65e'$	$-19.52a''_2$ $-21.51e'$	$-23.86e'$	$-23.35e'$
$-23.25a'_1$	$-20.07a'_1$ $-23.62a'_1$	$-27.32a'_1$	$-26.50a'_1$

a Vertical ionization potentials.
b Ref. 7.
c Indicates type and number of P ($3d$) orbitals in the basis set.
d Ref. 8.
e Ref. 9.
f Medium size basis set of Gaussian functions.
g Ref. 12.

TABLE II

Higher lying molecular orbitals of phosphorus pentafluoride

	Non-bonding π-type combinations		
a'_2	a''_2	$e'(2)$	$e''(2)$

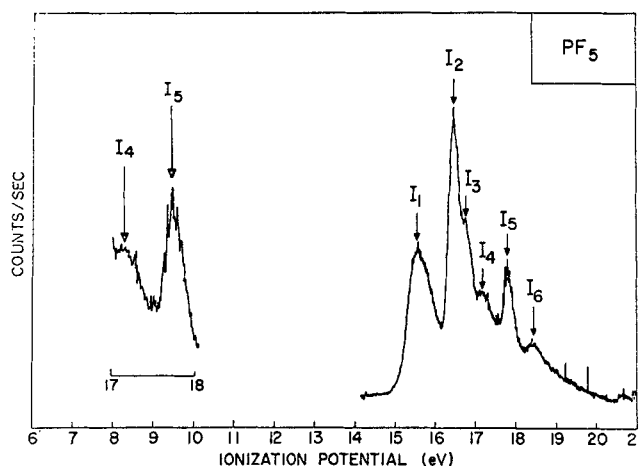| P-F($2p$) σ-bonding molecular orbitals		
$a'_1(2)$	a''_2	e''

FIGURE 2   He (I) photoelectron spectrum of phosphorus pentafluoride

Turning now to the pes of PF_5 (Figure 2) it is evident that the first two bands, I_1 and I_2, are of relatively high intensity. In turn this suggests that these bands are associated with the removal of electrons from the doubly degenerate orbitals. Employment of the energy argument which was presented above indicates that peaks I_1 and I_2 are best assigned to the e' and e'' non-bonding combinations of F ($2p$) orbitals. (Obviously pes offers no way of discriminating between MOs of symmetry e' and e''.) The shoulder I_3 and the peak which is designated I_4 are much less intense and consequently are assigned to singly degenerate non-bonding F ($2p$) π-type combinations of symmetry a''_2 and a'_2 respectively. The assignment of I_3 to a''_2 and I_4 to a'_2 is based on the MO calculations which uniformly placed the a''_2 MO at higher energy than the a'_2 MO. The peak which is labelled I_5 is of special interest since it possesses vibrational fine structure thereby implying the ionization of a bonding MO (*vide supra*). The vibrational spacing is 480 ± 80 cm^{-1}. Note that this number relates to the vibrational structure of the cation radical PF_5^+ and not to the neutral molecule PF_5. As expected

the force constants and vibrational frequencies are lower in the cation radical than in the neutral molecule, reductions of $\sim$ 5 to 10% being typical. On this basis the vibrational spacing of 480 ± 80 cm^{-1} in the cation radical corresponds to the value of 640 cm^{-1} in the ground state of PF_5. The 640 cm^{-1} frequency has been assigned[14] to the ν_2 (a'_1) F_{axial}-P-F_{axial} symmetrical stretching frequency thus implying that peak I_5 involves ionization of the corresponding F—P—F σ-bonding MO of symmetry a'_1. Particular attention is drawn to the deduction that the highest energy (least stable) P—F σ-bonding MO lies along the trigonal bipyramidal axis since such a conclusion is in accord with the three-center bonding model which has been proposed by Rundle[15] and Musher.[16] Intensity considerations suggest that peak I_6 involves the ionization of a singly degenerate orbital (however, due to the diminution of intensity near the 21.21 eV limit of He (I) pes it is impossible to be unequivocal on this point). Overall the pes spectrum of PF_5 agrees best with the medium size basis set *ab initio* MO calculation,[12] particularly when an empirical decrease of 8% is applied to the computed eigenvalues.[17] Since the singly degenerate F (2p) non-bonding combinations have already been assigned peak I_6 is ascribed tentatively to either the a'_1 or a''_2 P—F σ-bonding MO.

Attention will now be turned to the utility of pes in regard to a selction of stereochemical problems in phosphorus chemistry. The discovery[18] of a planar nitrogen geometry in $(CH_3)_2NPX_2$, X=F, Cl (Figure 3) prompted a surge of interest in the structural,[19] stereochemical,[20] and bonding[21] aspects of aminophosphines. Considerable interest has also been focused on the stereochemistry of the corresponding amino-substituted phosphoranes.[22] Very recently Trippett and coworkers[23] have demonstrated that the trigonal planar nitrogen geometry also persists in pentacoordinate compounds (Figure 4). It therefore seems safe to assume that the compounds that will be discussed below also possess planar nitrogen geometries. In hybridizational terms this implies that the nitrogen atom employs sp^2 hybrid orbitals in the sigma bonding framework and that the nitrogen lone pair resides in a pure $2p$ orbital.
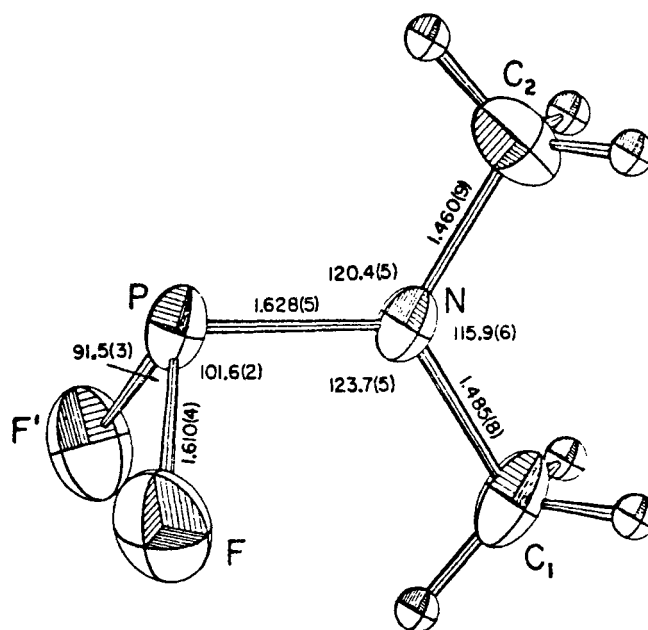

FIGURE 3   X-ray crystal structure of $(CH_3)_2NPF_2$.
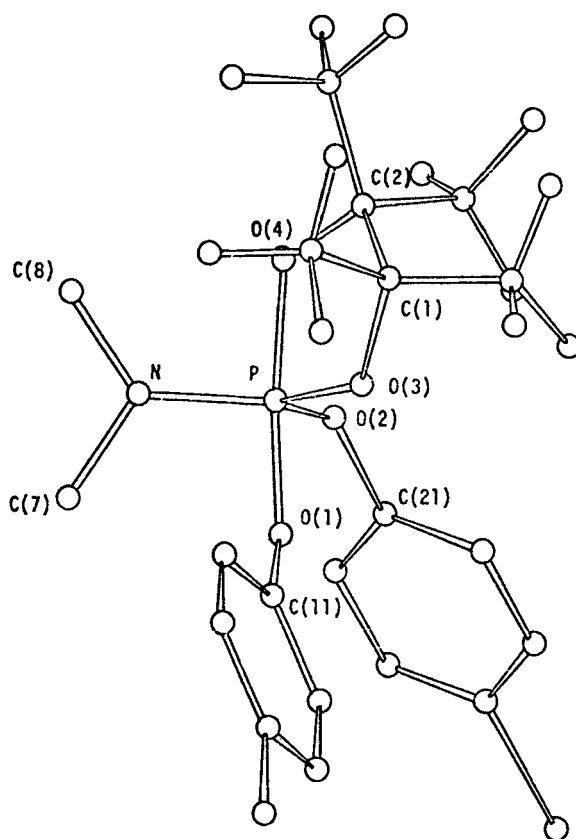
FIGURE 4   X-ray crystal structure of dimethylamino-substituted phosphorane.

TABLE III

pes Ionization potentials[a] for nitrogen and phosphorus lone pair orbitals in aminofluorophosphines and aminofluorophosphoranes

Compound	N lone pair	P lone pair
$(CH_3)_2NPF_4$	10.35	
H_2NPF_4	12.34	
$[(CH_3)_2N]_2PF_3$	8.84, 9.95	
$(H_2N)_2PF_3$	10.89, 12.09	
$[(CH_3)_2N]_3PF_2$	8.04, 9.03, 9.31	
$(CH_3)_2NPF_2$	9.58	10.48
$[(CH_3)_2N]_2PF$	8.18, 9.14	10.40
$[(CH_3)_2N]_3P$	7.61, 7.89, 8.86	9.98

[a]   Vertical ionization potentials in electron volts.
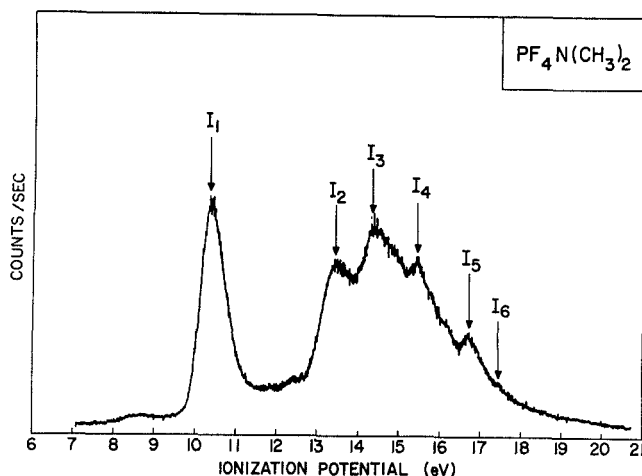
FIGURE 5   He (I) photoelectron spectrum of $(CH_3)_2NPF_4$.
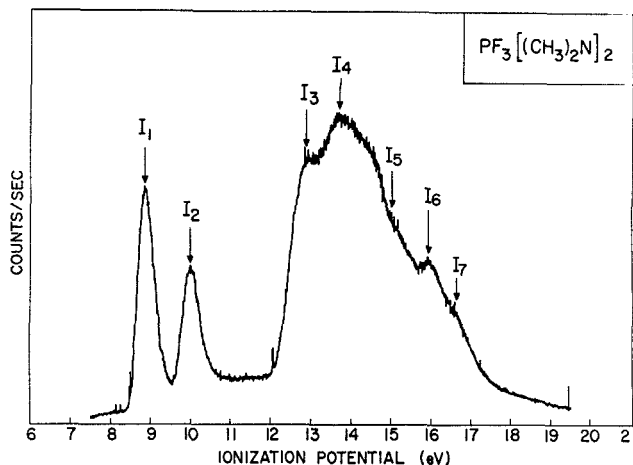
FIGURE 6   He (I) photoelectron spectrum of $[CH_3)_2N]_2PF_3$.

The pes of several amino- and dimethylamino-substituted phosphines and phosphoranes have been measured. A selection of such data is presented in Table III. The monoamine species, $(CH_3)_2NPF_4$ (Figure 5), H_2NPF_4, and $(CH_3)_2NPF_2$ exhibit single pes peaks at 10.35, 12.34 and 9.58 eV respectively. These peaks can be assigned unambiguously to ionization of the nitrogen lone pair electrons both on the basis of their line widths[24] and from consideration of inductive effects. Interestingly the *bis* (amino) species $[(CH_3)_2N]_2PF_3$ (Figure 6), $(H_2N)_2PF_3$, and $[(CH_3)_2N]_2PF$ exhibit ionizations of equal intensity in the nitrogen lone pair region, despite the fact that these lone pairs are chemically equivalent. The "lone pair splitting" arises because of the interaction of lone pairs through bonds and/or space.[25] More quantitatively, if the nitrogen lone pair orbitals are labelled n_1 and n_2 it is possible to write symmetric (+) and anti-symmetric (−) combinations,

$$\psi_+ = \frac{1}{\sqrt{2}} \ (n_1 + n_2) \qquad\qquad\qquad\qquad (5)$$

$$\psi_- = \frac{1}{\sqrt{2}} \ (n_1 - n_2) \qquad\qquad\qquad\qquad (6)$$

Consideration of the nodal rule[26] would place the ψ_+ combination at lower energy (i.e. more stable) than the ψ_- combination since the former has no nodes and the latter possesses one node. Thus, using the pes of $[(CH_3)_2 N]_2 PF_3$ as a specific example the 9.95 eV peak is assigned to ψ_+ whereas the peak at 8.84 eV is assigned to ψ_- . The difference in energy between these peaks (1.11 eV) is referred to as the "lone pair splitting". These nitrogen lone pair splittings become useful in a stereochemical sense when three N $(2p)$ orbitals are involved. In a trigonal bipyramidal phosphorane structure,[27] e.g. $[(CH_3)_2 N]_2 PF_3$, the three N $(2p)$ orbitals can be considered to be arranged either parallel to or perpendicular to the equatorial plane of the trigonal bipyramidal skeleton. Fortunately the group theoretical aspects of these possibilities (Figure 7) have already been worked out in an excellent series of papers by Walsh.[28] Nodal rule[26] considerations clearly indicate that for a horizontal arrangement of N $(2p)$ lone pairs the sequence of IPs should be $e' > a'_2$ while for the vertical arrangement of N $(2p)$ lone pairs the order is $a''_2 < e''$. In the case of the pes of $[(CH_3)_2 N]_3 PF_2$ (Figure 8) peak I_1 is assigned to the combination a-type symmetry and peaks I_2 and I_3 are assigned to the doubly degenerate e-type level. The foregoing assignments are based primarily on intensity considerations, further confirmation being provided by the Jahn-Teller splitting of the e-type level. Presumably Jahn-Teller degeneracy in the cation radical is removed by, for example, bending of the equatorial PN bonds (1).
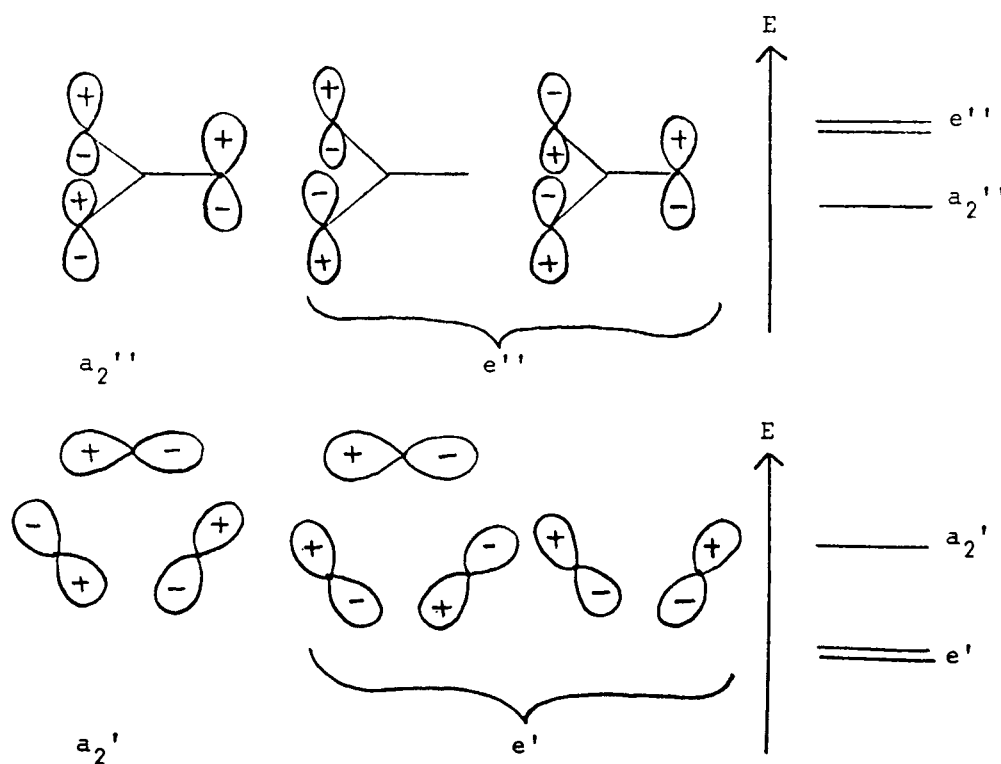

FIGURE 7   Horizontal and vertical combinations of nitrogen $2p$ orbitals in threefold symmetry.
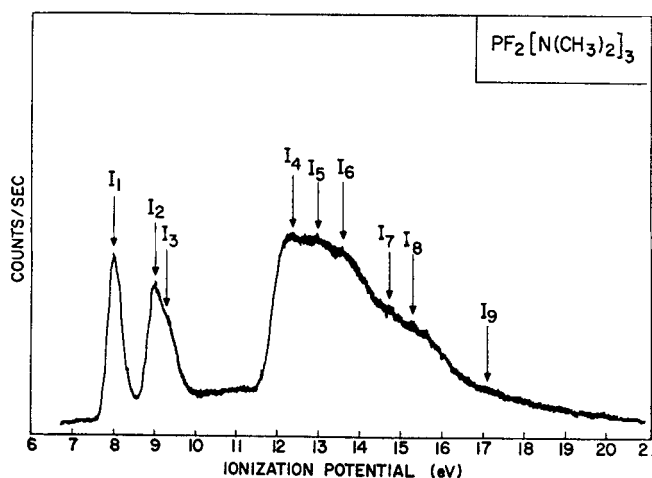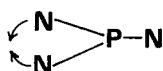
FIGURE 8   He (I) photoelectron spectrum of $[(CH_3)_2N]_3PF_2$.

1

The implication of this assignment is that the N $(2p)$ lone pair orbitals are arranged in the equatorial plane. This conclusion is consistent with the x-ray crystallographic result[23] mentioned above, theoretical considerations,[29] and nmr studies of aminophosphoranes[22h] and alkylthiophosphoranes.[30] It is interesting to note that it is not necessary to invoke P $(3d)$ orbital participation in order to explain the observed result.[29] Rather, the observed conformation follows from the fact that if the N $(2p)$ orbitals lie in the equatorial plane the lone pair bond pair repulsions are at $120°$ whereas these repulsions would be at $90°$ if the N $(2p)$ orbitals were parallel to the axial bonds.

The foregoing interpretation is consistent with that which has been presented for tris (dimethylamino) borane.[31] The two low energy bands are similar in shape to those of $[(CH_3)_2N]_3PF_2$ but inverted in energy. This implies that the lone pairs are arranged vertically in the boron compounds. Furthermore, this is the anticipated conformation in the sense that such an arrangement affords maximum overlap between the N $(2p)$ lone pair orbitals and the vacant B $(2p)$ orbital.

At first sight the pes of $[(CH_3)_2N]_3P$ (Figure 9) appears to resemble that of $[(CH_3)_2N]_3B$ in the sense that the sequence of nitrogen lone pair ionization potentials is $e > a$. This would imply a vertical (i.e. π-type) overlap of the N $(2p)$ lone pairs. However an electron diffraction study[18b] of $[(CH_3)_2N]_3P$ indicated that with the assumption of C_3 symmetry the dihedral angle between the nitrogen and phosphorus lone pairs is $60°$. In turn this implies that the lone pair interactions are more nearly horizontal than vertical. In order to resolve this apparent contradiction it is suggested that $[(CH_3)_2N]_3P$ may not in fact possess C_3 skeletal geometry. If the molecule has C_2 symmetry then one nitrogen lone pair can be arranged vertically and two can be arranged horizontally (Figure 10). In this manner the two horizontal nitrogen lone pairs a and b can interact with each other in the usual manner (vide supra) while the third nitrogen lone pair, c, will be raised in energy by a repulsive interaction with the phosphorus lone pair. Peaks I_1 and I_2, therefore, correspond to a near overlap of the a and c nitrogen lone pairs. The postulation of a repulsive interaction between a nitrogen lone pair and the phosphorus lone pair is also consistent with the relative insensitivity of the phosphorus lone pair to substituent electronegativity changes (Table III). This is particularly apparent in $(CH_3)_2NPF_2$ and

[(CH$_3$)$_2$N]$_2$PF. Interestingly the model which is proposed here for the ground state structure of [(CH$_3$)$_2$N]$_3$P is strikingly similar to the model which Mislow and coworkers have proposed[32] for the transition state for the interconversion of "propeller" molecules of the type (Ar)$_3$Z. Low temperature ^{13}C nmr and further structural studies of (R$_2$N)$_3$P molecules should prove to be very interesting.

Pes has also proved to be of value in conjunction with dynamic nmr stereochemical studies. For example, the origins of the P—N torsional barriers in aminophosphines are not well understood.[20d,e] There is clear evidence for the operation of steric effects and the importance of lone pair-lone pair repulsions seems to be indicated by the fact that H$_2$NPF$_2$ and (CH$_3$)$_2$NPF$_2$ adopt *gauche* ground state geometries.[18a,19b,d] Differential (i.e. axially unsymmetrical) nitrogen-phosphorus p_π-d_π bonding has also been suggested[20e] as a barrier contributor in an effort to explain the observation that unsymmetrical aminophosphines of the type R$_2$NPXY possess P—N rotational barriers which are 25-30% higher than those of the corresponding symmetrical compounds R$_2$NPX$_2$ and R$_2$NPY$_2$. Such a suggestion would also be consistent with the trigonal planar nitrogen geometries of H$_2$NPF$_2$ and (CH$_3$)$_2$NPF$_2$; however, it is worth noting that *ab initio* molecular orbital calculations on the model aminophosphine, H$_2$NPH$_2$, imply that the planarity at nitrogen is due to inductive rather than conjugative effects.[21b] In view of the foregoing it appeared to be worthwhile to investigate the pes of several series of symmetrical and unsymmetrical aminophosphines. The data for one such set are displayed in Table IV.[33] Note that the nitrogen lone pair IPs of (CH$_3$)$_2$NP(CF$_3$)$_2$, (CH$_3$)$_2$NP(Cl)CF$_3$, and (CH$_3$)$_2$NPCl$_2$ are essentially constant. This observation is consistent with a *gauche* ground state geometry for all three amino-phosphines i.e. an angle of ca. 90° between the nitrogen and phosphorus lone pairs since changes in the phosphorus lone pair energies have no significant effect on the nitrogen lone pair energies. Although the nitrogen lone pair IP for (CH$_3$)$_2$NP(Cl)(CF$_3$) is very slightly larger than that of (CH$_3$)$_2$NPCl$_2$ the pes data provide no evidence for the differential ($p \rightarrow d$) π bonding model since the nitrogen lone pair IP for (CH$_3$)$_2$NP(Cl)CF$_3$ is equal to that of (CH$_3$)$_2$NP(CF$_3$)$_2$.
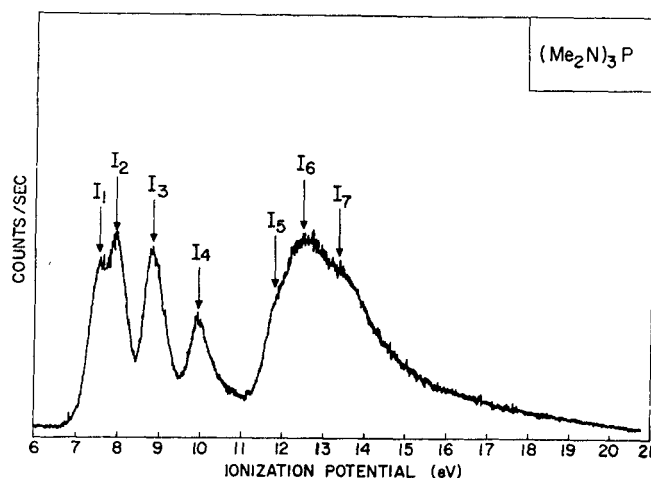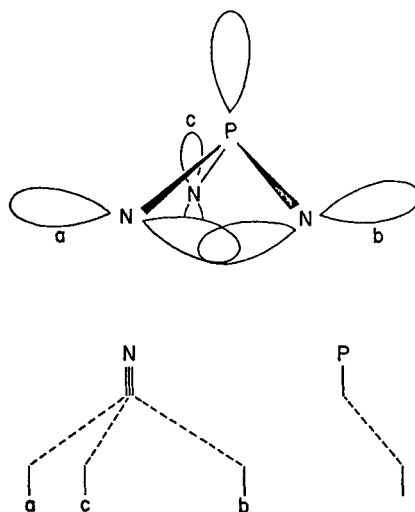

FIGURE 9   He (I) photoelectron spectrum of [(CH$_3$)$_2$N]$_3$P.

FIGURE 10   Lone pair interaction scheme for N_3P skeleton.

TABLE IV

Pes ionization potentials[a] for some aminophosphines

Compound	Nitrogen lone pair IP	Phosphorus lone pair IP	IP_P-IP_N	P—N torsional barrier[b,c]
$(CH_3)_2NP(CF_3)_2$	9.56	10.57	1.01	8.7
$(CH_3)_2NP(Cl)CF_3$	9.56	10.11	0.55	10.5
$(CH_3)_2NPCl_2$	9.45	9.96	0.51	8.4

[a] Vertical ionization potentials in electron volts.
[b] See reference 20e.
[c] In kcal/mol.

Assuming *gauche* ground state geometries for $(CH_3)_2NP(CF_3)_2$, $(CH_3)_2NP(Cl)CF_3$, and $(CH_3)_2NPCl_2$ the differences in the phosphorus and nitrogen lone pair IPs, IP_P-IP_N, are important in stressing the magnitude of the lone pair interactions since according to perturbation theory the splitting, δE, between two interacting levels, E_1 and E_2, is given by

$$\delta E = \frac{\beta_{NP}}{\Delta E},$$

where $\Delta E = E_1 - E_2$ $(E_1 < E_2)$ and β_{NP} is a lone pair interaction parameter.[34] On this basis the order of lone pair-lone pair repulsions is $(CH_3)_2NPCl_2 = (CH_3)_2NP(Cl)CF_3 > (CH_3)_2NPCl_2$. By contrast the order of steric effects is $(CH_3)_2NP(CF_3)_2 > (CH_3)_2NP(Cl)CF_3 > (CH_3)_2NPCl_2$. The observed sequence of P—N torsional barriers $(CH_3)_2NP(Cl)CF_3 > (CH_3)_2NP(CF_3)_2 = (CH_3)_2NPCl_2$ could clearly result from the combination of lone pair-lone pair repulsion and steric effects of approximately equal magnitude.

One of the great advantages of pes is its inherently rapid time scale. The technique is, therefore, ideally suited for the detection of individual conformers in a conformational mixture. Our initial experiments in this area have been concerned with the conformations of A_2X_4 molecules. In fact the stereochemistry of

hydrazines and their heavier congeners has been a subject of interest for four decades.[35] With few exceptions[36] acyclic hydrazines adopt the *gauche* conformation[37] (Figure 11). However the stereochemistry of diphosphines[38] and diarsines[3a] is of particular interest since the *gauche* and *trans* rotamers appear to be of comparable energy. This raised the intriguing possibility that one might be able to detect the concomitant presence of both rotamers by means of pes.
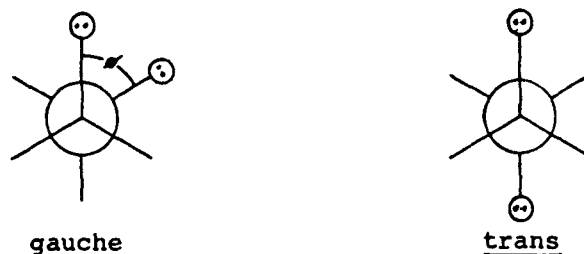

gauche   trans

FIGURE 11   *Gauche* and *trans* rotamers for $A_2 X_4$ molecules.

In general the interaction between the A lone pairs of $A_2 X_4$ molecules is anticipated to exhibit a dependence on the dihedral angle ϕ such that the lone pair splitting Δ should be *trans* $\gg$ *gauche*.[36e,40] Thus, for example, MINDO/2 calculations on $N_2 H_4$ (Ref. 41) indicate that the energies of the two lone pair MOs, E_{n+} and E_{n-}, vary continuously with the dihedral angle ϕ. Thus, at $\phi = 0$ n_- lies 1.45 eV above n_+, at $\phi = 80°$ n_+ and n_- possess the same energy, while at $180°$ n_- lies 2.41 eV below n_+.

In the diphosphines and diarsines studies here[42] it was therefore anticipated that the lone pair splitting of the *trans* rotamers would be 1-2 eV, while the lone pair splitting of the *gauche* rotamer should be approximately 0 eV. On this basis the peaks labelled I_1 and I_3 in the pes of $(CH_3)_4 P_2$ (Figure 12) are assigned to the n_+ and n_- phosphorus lone pair combinations of the *trans* rotamer. The remaining peak (I_2) in the phosphorus lone pair region is therefore ascribed to the *gauche* rotamer. Note that this interpretation is internally self consistent in the sense that the lone pair ionization potential for the *gauche* rotamer and the mean of the lone pair IPs for the *trans* rotamers are very similar. In turn these values are close to the lone pair IP of $(CH_3)_2 PH$ (Table V), an observation which is anticipated on the basis of the similarities of the electronegativities of the $(CH_3)_2 P$ and H moieties.[43] The fact that the mean lone pair IP for the *trans* rotamer is slightly less than that of the *gauche* rotamer is attributed to the net destabilizing effect of the *trans* lone pair interaction.
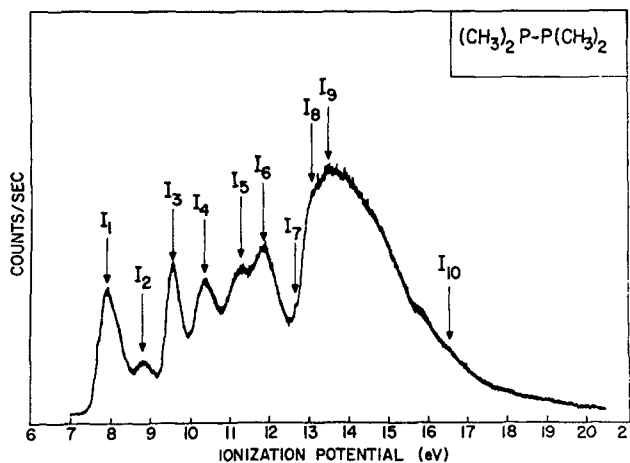

FIGURE 12   He (I) photoelectron spectrum of $(CH_3)_4 P_2$.

TABLE V

Pes ionization potential[a] data for diphosphines and diarsines

Compound		Abundance (%)	Lone pair IPs	Δ	Average lone pair IP	P–P or As–As[b]	P–C or As–C[b]
gauche	$(CH_3)_4P_2$	16	8.79	–	8.79	10.33	11.22, 11.83
trans	$(CH_3)_4P_2$	84	7.88, 9.54	1.66	8.71	10.33	11.22, 11.83
gauche	$(CH_3)_4As_2$	12	8.85	–	8.85	9.82	10.60, 11.21
trans	$(CH_3)_4As_2$	88	7.91, 9.50	1.59	8.70	9.82	10.60, 11.21
gauche	$(CF_3)_4P_2$	10	11.57	–	11.57	13.09	13.49
trans	$(CF_3)_4P_2$	90	10.71, 12.11	1.45	11.44	13.09	13.49
trans	$(CF_3)_4As_2$	100	10.39, 11.94	1.55	11.17	12.07	12.58
	$(CH_3)_2PH$	100	9.13	–	9.13	–	11.75
	$(CH_3)_2AsH$	100	9.14	–	9.14	–	11.16, 11.54
	$(CF_3)_2PH$	100	11.51	–	11.51	–	13.22

[a] Vertical ionization potentials in electron volts.
[b] σ-bond.

Analogous assignments can be made for the ionizations of $(CH_3)_4As_2$ (Figure 13). Note that the *trans* lone pair splittings of $(CH_3)_4P_2$ and $(CH_3)_4As_2$ are similar. As with $(CH_3)_4P_2$ the mean lone pair IP for the *trans* and the lone pair IP for the *gauche* rotamer agree with each other and are comparable to that of $(CH_3)_2AsH$ (Table V).[44]
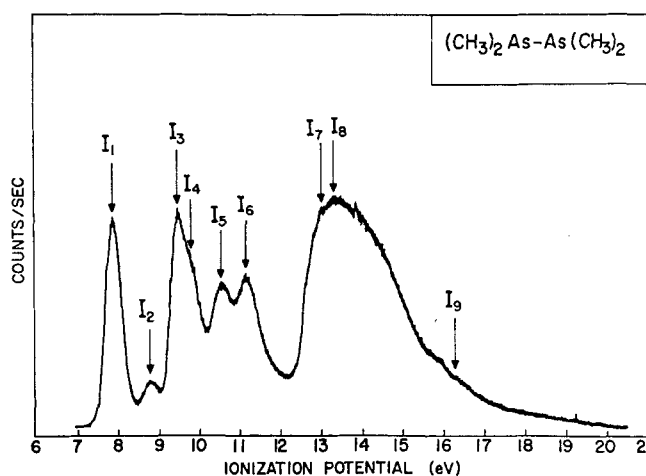

FIGURE 13   He (I) photoelectron spectrum of $(CH_3)_4As_2$.

The assignments for the *trans* and *gauche* rotamers of $(CF_3)_4P_2$ follow from the foregoing arguments. Similar comments apply to the average of the *trans* lone pair IPs, the *gauche* lone pair IP of $(CF_3)_2PH$ (Table I). In the case of $(CF_3)_4As_2$ no *gauche* rotamer was detectable by pes; the assignments in Table V were made by analogy with those for $(CF_3)_4P_2$.

The percentage compositions of the rotameric mixtures (Table V) were computed from the relative peak areas. This approach is based on: (a) the validity of the foregoing assignments; and (b) the assumption that the area under a pes peak is proportional to the abundance of the rotamer. In fact such an assumption may not be generally valid since, as pointed out earlier, photoionization cross sections are dependent upon several factors such as the symmetry and orbital character of the MO from which the electron is removed, and the

relative energies of the light source and the MO in question.[5] However, in the case of the ionization of the lone pair MOs, the *trans* and *gauche* rotamers of hydrazine-like molecules this assumption is reasonable because the orbitals are close in energy and similar in character. While the actual percentage compositions in Table V differ from those estimated by vibrational spectroscopy[45] for $(CH_3)_4P_2$, $(CF_3)_4P_2$,[38d] and $(CH_3)_4As_2$ (Ref. 39b) the qualitative trends in the pes data substantiate the generalizations that have been made for A_2X_4 species,[45] viz. the *trans* conformer is favored by: (a) increasing the A—A bond distance; and (b) increasing the electronegativity of X. The pes results however are not in accord with the electron diffraction study of $(CH_3)_4P_2$ which indicated that this molecule exists exclusively in the *trans* conformation.[38b] Despite the steric bulk of the C_6F_5 moiety the fact that no *gauche* rotamer is detectable in $(CF_3)_4As_2$ (by pes or vibrational spectroscopy[39c]) contrasts sharply with the claim[39a] that $(C_6F_5)_4As_2$ can be separated into *gauche* and *trans* rotamers.

The final part is concerned with the utility of pes in regard to some bonding problems in phosphorus chemistry. Polyphosphines have elicited considerable attention[46] from the standpoint of developing an appropriate bonding description. Unlike their monophosphine analogs polyphosphines exhibit intense UV absorption. This observation has been attributed by some authors[47] to the delocalization of phosphorus lone pair electrons into formally vacant $3d$ (and presumably $4p$) orbitals of juxtaposed phosphorus atoms. The π-bonding model has been questioned however on both structural[48] and electronegativity[49] grounds. It therefore seemed appropriate to investigate the pes of a selection of polyphosphines.[50]

The observation of more than one peak in the phosphorus lone pair region of the pes of a cyclopolyphosphine can be attributed to interactions between the phosphorus lone pairs. In the case of $(CF_3P)_4$ the molecular symmetry is known[51] to be D_{2d}, hence the MOs derived from the lone pairs are of symmetry b_2, e, and a_1 having the forms indicated in Figure 14. In a_1 all four nearest neighbor interactions are antibonding, in b_2 all are bonding, while in e all such interactions are nonbonding. The order of increasing orbital energy, and so of decreasing ionization potential, should therefore be $b_2 > e > a_1$. Furthermore, the transannular interactions in a_1 and b_2 are bonding but in e antibonding; the a_1-e separation should therefore be less than the e-b_2 one. The first three ionization potentials (I_1, I_2, I_3) follow this pattern and can be assigned respectively to a_1, e and b_2 (Figure 15). The observed ionization potentials lead to the following interaction parameters:

$$\beta_{12}, 1.10 \text{ eV}; \quad \beta_{13}, 0.70 \text{ eV} .$$

Note also that I_2 is more intense than I_1 or I_3, as would be expected since the e level is doubly degenerate.
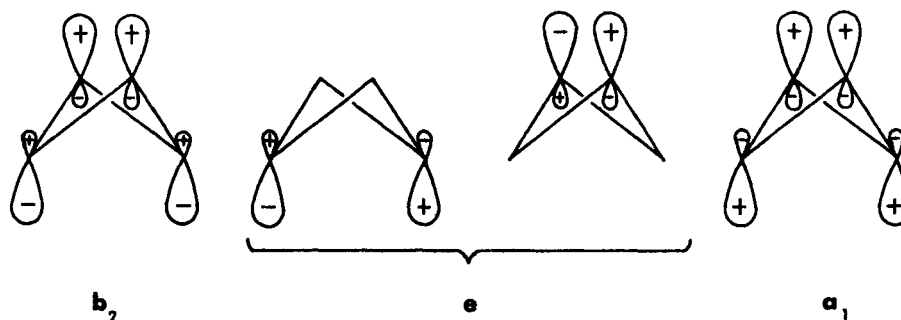

FIGURE 14   Combinations of phosphorus lone pair orbitals in D_{2d} symmetry.

The next two pes peaks (I_4, I_5) can be assigned to ionization of P—P and P—C σ bonds respectively by comparison with the corresponding peaks in $(CF_3)_4P_2$ (Ref. 42) and $(CF_3)_3P$. Since the cyclopentaphosphine $(CF_3P)_5$ is devoid of symmetry,[52] five nondegenerate lone pair ionizations are anticipated. The first five pes peaks of $(CF_3P)_5$ (Figure 16) are therefore assigned to phosphorus lone pair ionizations. Arguing by analogy with the pes of $(CF_3P)_4$, $(CF_3)_4P_2$, and $(CF_3)_3P$ (Table VI) the most reasonable assignment for peak I_8 (13.89 eV) is ionization of the P—C σ bond. In turn this implies that peaks I_6 and I_7 (12.32 and 12.67 eV) are
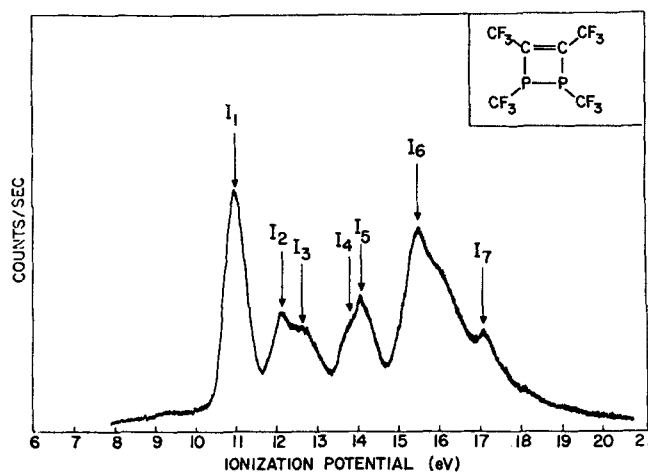
FIGURE 15   He (I) photoelectron spectrum of $(CF_3P)_4$.
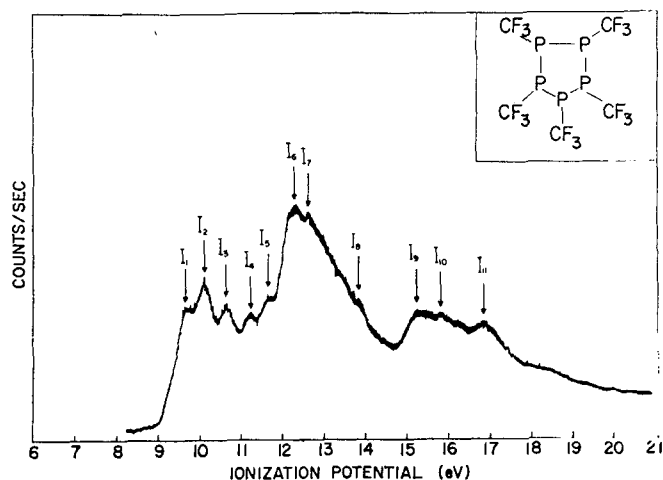
due to ionization of the P—P σ bonds. The observation of two such peaks is consistent with the wide scatter of P—P bond distances in $(CF_3P)_5$.[52]

Arguments analogous to the foregoing have been used to assign the phosphorus lone pair and the P—P and P—C σ bond ionizations in the heterocyclic polyphosphine $(CF_3)_2 C_2 P_2(CF_3)_2$. (Table VI and Figure 17.) The remaining low energy peak (I_2, 12.14 eV) is therefore ascribed to ionization of the carbon-carbon double bond. The observation of two peaks (I_4 and I_5) in the P—C σ bond region is presumably due to the fact that $(CF_3)_2 C_2 P_2(CF_3)_2$ contains both endo- and exocyclic P—C bonds.

The pes bands of the hybrid diphosphine $(CF_3)_2 PP(CH_3)_2$ can be assigned unambiguously by comparison with those of the two corresponding symmetrical diphosphines $(CF_3)_4 P_2$ and $(CH_3)_4 P_2$ (Table VI).
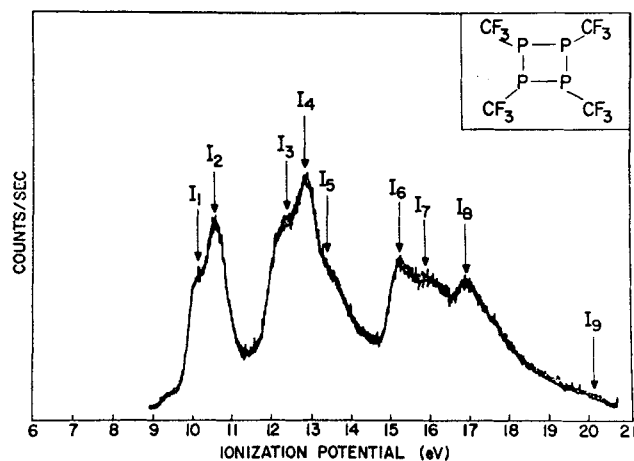
FIGURE 17   He (I) photoelectron spectrum of $(CF_3)_2C_2P_2(CF_3)_2$.

TABLE VI
Pes ionization potential[a] data for polyphosphines and $(CF_3)_3P$

Compound	Lone pair IPs	Mean lone pair IP	P–P σ-bond	P–C σ-bond	Other
$(CF_3P)_4$	10.18, 10.58, 12.38	10.93	12.89	13.50	—
$(CF_3)_4P_2$ (*trans*)[b]	10.71, 12.11	11.44	13.09	13.49	—
$(CF_3)_3P$	11.70	11.70	—	13.52	—
$(CF_3P)_5$	9.71, 10.16, 10.70, 11.21, 11.73	10.70	12.32, 12.67	13.89	—
(structure)	10.97	10.97	12.62	13,78, 14.11	C=C, 12.11
$(CF_3)_2PP(CH_3)_2$	9.37, 10.38	9.88	11.64	11.64, 13.29	
$(CH_3)_4P_2$ (*trans*)[b]	7.88, 9.54	8.71	10.33	11.22, 11.33	

[a] Vertical ionization potentials in electron volts.
[b] Similar data were obtained for the *gauche* rotamer. See Ref. 42.

Since the interactions between the phosphorus lone pair MOs does not alter their total energy, the average lone pair binding energy in a polyphosphine should be equal to minus the average of the corresponding IPs. The values found in this way (allowing for the degeneracy of I_2 in $(CF_3P)_4$) are shown in Table VI. It will be seen that those for $(CF_3)_3P$, $(CF_3)_4P_2$, $(CF_3P)_4$, and $(CF_3P)_5$ can be quite well explained in terms of a simple inductive effect by the CF_3 groups. Thus the average values rise in the order $(CF_3P)_4 \sim (CF_3P)_5 < (CF_3)_4P_2 < (CF_3)_3P$, and while extrapolation of the values for $(CF_3P)_4$, $(CF_3)_4P_2$, and $(CF_3P)_5$ leads to an estimate (12.06 eV) for $(CF_3)_3P$ which is larger than that (11.70 eV) observed, the difference is small and could very

well be due to increased bond angles at phosphorus, and consequent increase in lone pair s character, in $(CF_3)_3P$. If $p_\pi{:}d_\pi$ bonding were important, it would increase the lone pair binding energy in $(CF_3P)_4$, $(CF_3)_4P_2$, and $(CF_3P)_5$ relative to $(CF_3)_3P$. Our results therefore indicate that such bonding must be relatively unimportant.

The mean lone-pair binding energies of the other compounds listed in Table VI also seem to follow a simple inductive pattern. Thus the values for $(CF_3P)_4$ and $(CF_3)_2C_2P_2(CF_3)_2$ are almost identical, as would be expected on this basis, and that for the hybrid diphosphine, $(CF_3)_2PP(CH_3)_2$ is close to the mean (10.07 eV) of the values for the symmetrical species $(CF_3)_4P_2$ and $(CH_3)_4P_2$. Note also that only one lone pair signal was obtained from the heterocyclic compound $(CF_3)_2C_2P_2(CF_3)_2$ implying that the two lone pair AOs must be orthogonal and also that they are not significantly coupled to the double bond. The structure of $(CF_3)_2C_2P_2(CF_3)_2$ has not yet been determined our results indicate that it must have C_2 symmetry with *trans* PCF$_3$ groups.

ACKNOWLEDGMENT

REFERENCES

1.   For reviews see, for example: (a) C. R. Brundle and M. B. Robin in *Determination of Organic Structures by Physical Methods* (F. C. Nachod and J. J. Zuckerman, Eds.) (Academic Press, New York, 1971) Vol. III; (b) H. Bock and B. G. Ramsey, *Angew. Chem. Intern. Ed. Engl.* 12, 734 (1973).

2.   D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, *Molecular Photoelectron Spectroscopy* (Wiley-Interscience, London, 1970).

3.   The He (I) pes apparatus which was employed in the present work was designed and constructed at the University of Texas at Austin. The design was similar to that described by Turner (Ref. 2). See D. W. Goodman, Ph.D. dissertation, The University of Texas at Austin, December 1973, and P. Bishop, M. J. S. Dewar, and D. W. Goodman, to be published.

4.   T. Koopmans, *Physica* 1, 104 (1934).

5.   (a) L. L. Lohr, Jr. and M. B. Robin, *J. Am. Chem. Soc.* 92, 7241 (1970); (b) W. Theil, Ph.D. dissertation, Philipps Universitat, Marburg, Lahn, W. Germany, 1973.

6.   D. W. Goodman, M. J. S. Dewar, J. R. Schweiger, and A. H. Cowley, *Chem. Phys. Lett.* 21, 474 (1973).

7.   R. S. Berry, M. Tamres, C. J. Ballhausen, and H. Johansen, *Acta Chem. Scand.* 22, 231 (1968).

8.   R. D. Brown and J. B. Peel, *Australian J. Chem.* 21, 2605, 2617 (1972).

9.   J. B. Florey and L. C. Cusachs, *J. Am. Chem. Soc.* 94, 2617 (1972).

10.   P. C. van der Voorn and R. S. Drago, *J. Am. Chem. Soc.* 88, 3255 (1966).

11.   D. P. Santry and G. A. Segal, *J. Chem. Phys.* 47, 158 (1967).

12.   A. Strich and A. Veillard, *J. Am. Chem. Soc.* 95, 5574 (1973).

13.   K. W. Hansen and L. S. Bartell, *Inorg. Chem.* 4, 1775 (1965).

14.   J. E. Griffiths, R. P. Carter, Jr., and R. R. Holmes, *J. Chem. Phys.* 41, 863 (1964).

15.   R. E. Rundle, *J. Am. Chem. Soc.* 85, 112 (1963); R. E. Rundle, *Surv. Progr. Chem.* 1, 81 (1963).

16.   J. I. Musher, *Angew. Chem. Int. Ed. Engl.* 8, 54 (1969).

17.   (a) H. Basch, M. B. Robin, N. A. Kuebler, C. Baker, and D. W. Turner, *J. Chem. Phys.* 51, 52 (1969); (b) C. R. Brundle, D. W. Turner, M. B. Robin, and H. Basch, *Chem. Phys. Lett.* 3, 292 (1969); (c) C. R. Brundle, M. B. Robin, and H. Basch, *J. Chem. Phys.* 53, 2196 (1970).

18.   (a) E. D. Morris and C. E. Nordman, *Inorg. Chem.* 8, 1673 (1969); (b) L. V. Vilkov, L. S. Khaikin, and V. V. Evdokimov, *Zh. Strukt. Khim.* 10, 1101 (1969).

19.   (a) G. C. Holywell, D. W. K. Rankin, B. Beagley, and J. M. Freeman, *J. Chem. Soc. A*, 785 (1971); (b) A. H. Brittain, J. E. Smith, P. L. Lee, K. Cohn, and R. H. Schwendeman, *J. Am. Chem. Soc.* 93, 6772 (1971); (c) J. R. Durig and J. M. Casper, *J. Cryst. Mol. Struct.* 2, 1 (1972); (d) P. Forti, D. Damiami, and P. G. Favero, *J. Am. Chem. Soc.* 95, 756 (1973).

20.   (a) M. P. Simmonin, J. J. Basselier, and C. Charrier, *Bull. Soc. Chim. Fr.* 3544 (1967); (b) A. H. Cowley, M. J. S. Dewar, and W. R. Jackson, *J. Am. Chem. Soc.* 90, 4185 (1968); (c) D. Imberry and H. Freibolin, *Z. Naturforsch.* B 236, 759 (1968); (d) H. Goldwhite and D. G. Rowsell, *Chem. Commun.* 713 (1969); (e) A. H. Cowley, M. J. S. Dewar, W. R. Jackson, and W. B. Jennings, *J. Am. Chem. Soc.* 92, 1085, 5206 (1970); (f) M. P. Simmonin, C. Charrier, and

R. Burgada, *Org. Magn. Reson.* 4, 113 (1972); (g) M. P. Simmonin, R. M. Lequan, and F. W. Wehrili, *J. Chem. Soc., Chem. Commun.* 1204 (1972); (h) S. DiStefano, H. Goldwhite, and E. Mazzola, *Org. Magn. Resonance* 6, 1 (1974).

21. (a) M. C. Bach, F. Crassier, J. F. Labarre, and C. Leibovici, *J. Mol. Structure* 13, 171 (1972); (b) I. G. Csizmadia, L. M. Tel, A. H. Cowley, M. W. Taylor, and S. Wolfe, *J. Chem. Soc., Chem. Commun.* 1147 (1972); (c) M. C. Labarre and Y. Coustures, *J. Chim. Phys.* 70, 534 (1973); (d) M. C. Bach, C. Brain, F. Crasnier, J. B. Labarre, C. Leibovici, and A. Dargelos, *J. Mol. Structure* 17, 23 (1973); (e) F. Mathis, L. Lafaille, and R. Burgada, *Spectrochim. Acta* 30 A, 357 (1974); (f) I. G. Csizmadia, A. H. Cowley, M. W. Taylor, and S. Wolfe, *J. Chem. Soc., Chem. Commun.* 432 (1974).

22. (a) E. L. Mutterties, W. Mahler, K. J. Packer, and R. Schmutzler, *Inorg. Chem.* 3, 1298 (1964); (b) M. A. Landau, V. V. Sheluchenko, G. I. Drozd, S. S. Dubov, and S. Z. Ivin, *Zh. Strukt. Khim.* 8, 1097 (1967); (c) F. N. Tebbe and E. L. Muetterties, *Inorg. Chem.* 7, 172 (1968); (d) V. V. Sheluchenko, M. A. Sokalskii, M. A. Landau, G. I. Drozd, and S. S. Dubov, *Zh. Strukt. Khim.* 10, 142 (1969); (e) M. A. Sokalskii, G. I. Drozd, M. A. Landau, and S. S. Dubov, *Zh. Strukt. Khim.* 10, 1113 (1969); (f) J. D. Harman and D. W. A. Sharp, *Inorg. Chem.* 10, 1538 (1971); (g) M. J. C. Hewson, S. C. Peake, and R. Schmutzler, *Chem. Commun.* 1454 (1971); (h) E. L. Muetterties, P. Meakin, and R. Hoffmann, *J. Am. Chem. Soc.* 94, 5674 (1972); (i) A. H. Cowley and J. R. Schweiger, *J. Chem. Soc., Chem. Commun.* 560 (1972).

23. S. Trippett, private communication. The author is indebted to Professor Trippett for these x-ray crystallographic data.

24. In all the trivalent nitrogen-phosphorus compounds which have been measured so far the phosphorus lone pair ionizations have been broader than the nitrogen lone pair ionizations.

25. For an excellent review of the phenomena of the interactions of lone pairs and multiple bonds see R. Hoffmann, *Accounts Chemical Research* 4, 1 (1971). Further experiments in our laboratory are aimed at evaluation of the relative importance of the through bond and through space mechanisms.

26. See, for example, E. Heilbronner and H. Bock, *Das HMP-Modell und seine Anwendung* (Verlag Chemie, Weimheim, 1969-70), Vols. I-III.

27. Recent x-ray crystallographic studies have established that certain spiro oxyphosphoranes and 1,3,2-dioxaphospholanes possess square pyramidal structures. See J. A. Howard, D. R. Russell, and S. Trippett, *J. Chem. Soc. Chem. Commun.* 856 (1973); and H. Wunderlich, D. Mootz, R. Schmutzler, and M. Wieber, *Z. Naturforsch.*, in press. However, all acyclic phosphoranes are expected to possess a trigonal bipyramidal structure. See R. R. Holmes, *J. Am. Chem. Soc.* 96, 4143 (1974) and references therein.

28. A. D. Walsh, *J. Chem. Soc.* 2301 (1953).

29. For a discussion of the relative importance of lone pair-lone pair repulsions and P (3*d*) orbital effects in phosphoranes, see R. Hoffmann, J. M. Howell, and E. L. Muetterties, *J. Am. Chem. Soc.* 94, 3047 (1972). See also Ref. 12.

30. (a) S. C. Peake and R. Schmutzler, *Chem. Commun.* 1662 (1968); (b) S. C. Peake and R. Schmutzler, *J. Chem. Soc.* A 1049 (1970).

31. H. Bock and W. Fuss, *Chem. Ber.* 104, 1687 (1971).

32. P. Finocchiaro, D. Gust, and K. Mislow, *J. Am. Chem. Soc.* 96, 2176 (1974).

33. A. H. Cowley, M. J. S. Dewar, J. W. Gilje, D. W. Goodman, and J. R. Schweiger, *J. Chem. Soc., Chem. Commun.* 340 (1974).

34. See, for example, M. J. S. Dewar, *Hyperconjugation* (Ronald Press, New York, 1962).

35. For some representative articles see: (a) W. G. Penney and G. B. B. M. Sutherland, *J. Chem. Phys.* 2, 492 (1934); (b) M. J. S. Dewar and W. B. Jennings. *J. Chem. Phys.* 91, 3655 (1969); (c) S. F. Nelsen and J. M. Buschek, *J. Am. Chem. Soc.* 95, 2011 (1973); (d) S. F. Nelsen, J. M. Buschek, and P. J. Hintz, *J. Am. Chem. Soc.* 95, 2013 (1973). J. M. Buschek, and P. J. Hintz, *J. Am. Chem. Soc.* 95, 2013 (1973).

36. (a) C. B. Colburn, F. A. Johnson, and C. Hanvey, *J. Chem. Phys.* 43, 4526 (1965); (b) J. R. Durig and J. W. Clark, *J. Chem. Phys.* 48, 3216 (1968); (c) D. F. Koster and F. A. Miller, *Spectrochim. Acta* 24 A, 1487 (1968); M. J. Cardillo and S. H. Bauer, *Inorg. Chem.* 8, 2086 (1969); (e) P. Rademacher, *Angew. Chem. Intern. Ed. Engl.* 12, 408 (1973).

37. For an excellent discussion of the "gauche effect" see S. Wolfe, *Accounts Chem. Res.* 5, 102 (1972).

38. See, for example: (a) J. R. Durig and J. S. DiYorio, *Inorg. Chem.* 8, 2796 (1969); (b) A. McAdam, B. Beagley, and T. G. Hewitt, *Trans. Faraday Soc.* 66, 2732 (1970); (c) J. R. Durig and R. W. MacNamee, *J. Mol. Structure* 17, 426 (1973); (d) J. D. Witt, J. W. Thompson, and J. R. Durig, *Inorg. Chem.* 12, 811 (1973).

39. (a) M. Green and D. Kirkpatrick, *Chem. Commun.* 57 (1967); (b) J. R. Durig and J. M. Casper, *J. Chem. Phys.* 55, 198 (1971); (c) J. W. Thompson, J. D. Witt, and J. R. Durig, *Inorg. Chem.* 12, 2124 (1973).

40. M. J. S. Dewar, *J. Am. Chem. Soc.* 74, 3345 (1952).

41. N. Bodor, M. J. S. Dewar, A. Harget, and E. Haselbach, *J. Am. Chem. Soc.* 92, 3854 (1970).

42. A. H. Cowley, M. J. S. Dewar, D. W. Goodman, and M. C. Padolina, *J. Am. Chem. Soc.* 96, 2648 (1974).

43. J. E. Huheey, *J. Phys. Chem.* 69, 3284 (1965).

44. The close correspondence of the lone pair IPs of the P and As compounds in Table V is consistent with the pes data for PH_3 and AsH_3. See G. R. Branton, D. C. Frost, C. A. McDowell, and I. A. Stenhouse, *Chem. Phys. Lett.* 5, 1 (1970).

45. This approach is based on the assumption that Raman peak intensities are proportional to the abundances of the rotamers. This assumption is clearly questionable since the dipole moments of the two rotamers must differ and their derivatives should differ likewise.

46. For reviews see, for example: (a) L. Maier, *Progr. Inorg. Chem.* 5, 27 (1963); (b) J. E. Huheey, *J. Chem. Educ.* 40, 153 (1963); (c) A. H. Cowley, *Chem. Rev.* 65, 617 (1965); (d) A. H. Cowley and R. P. Pinnell, *Topics Phosphorus Chemistry* 4, 1 (1967); (e) E. Fluck, *Preparative Inorg. Reactions* 5, 103 (1968); (f) A. H. Cowley, *Compounds Containing Phosphorus-Phosphorus Bonds* (Dowden, Hutchinson, and Ross, Inc. Stroudsburg, Pa., 1973).

47. (a) W. Mahler and A. B. Burg, *J. Am. Chem. Soc.* **80**, 6161 (1958); (b) L. R. Grant and A. B. Burg, *J. Am. Chem. Soc.* **84**, 1835 (1962).
48. R. L. Kuczkowski, H. W. Schiller, and R. W. Rudolph, *Inorg. Chem.* **10**, 2505 (1971).
49. H. W. Schiller and R. W. Rudolph, *Inorg. Chem.* **10**, 2500 (1971).
50. A. H. Cowley, M. J. S. Dewar, D. W. Goodman, and M. C. Padolina, *J. Am. Chem. Soc.* **96**, 3666 (1974).
51. C. J. Palenik and J. Donohue, *Acta Cryst.* **15**, 564 (1962).
52. C. J. Spencer and W. N. Lipscomb, *Acta Cryst.* **14**, 250 (1961).