Russian Chemical Reviews, **46** (9), 1977

Translated from *Uspekhi Khimii*, **46**, 1515-1543 (1977)

U.D.C. 543.42 : 547.1.118

The Photoelectron Spectroscopy of Organophosphorus Compounds

V.V.Zverev and Yu.T.Kitaev

The applications of the method of photoelectron spectroscopy in the study of the electronic and steric structures of organophosphorus compounds is examined. The spectra of two-, three-, and four-coordinated phosphorus are interpreted in terms of the approximation of Koopmans' theorem. Attention is concentrated on the elucidation of the composition of the upper occupied orbitals. The manifestations of the $n-\pi$ and $n-n$ interactions in the photo-electron spectra of these compounds are investigated.
The bibliography includes 104 references.

CONTENTS

I.	Introduction	791
II.	λ^3-phosphorins	792
III.	Compounds of three-coordinated phosphorus	795
IV.	Compounds of four-coordinated phosphorus	802

I. INTRODUCTION

The ultraviolet photoelectron spectroscopy (PES) is a unique method whereby it is possible to establish the sequence of the ionisation potentials of molecules. The first reports showing that the photoelectron spectrum contains information about the set of ionisation potentials were published by Vilesov et al.[1] and Turner and Al-Joboury[2] more than ten years ago, but the period of the most intense development of the method covers the last five years. The method of X-ray (photo)electron spectroscopy, which permits the determination of the electron binding energies in the inner non-valence levels, was developed somewhat earlier[3], but the survey of the available information about the applications of this method in the study of organophosphorus molecules is outside the scope of the present review.

This review deals with the applications of the PES method in the study of the compositions of the upper occupied molecular orbitals and of the steric structures of organophosphorus compounds. The photoelectron spectra of phosphorus compounds have been obtained by many groups of investigators and the number of compounds which have been investigated is fairly large.

The method of ultraviolet PES, described in a number of reviews and monographs (see, for example, Refs. 4–9), has become firmly established in organic chemistry. The most important results have been obtained by the PES method in the study of the $\pi-\pi$ interaction in conjugated and non-conjugated molecules with π bonds[10,11], the $\pi-\sigma$ mixing of orbitals in non-planar molecules[12,13], the problem of the $\pi-\sigma$ separation in planar conjugated systems[14,15], the $n-n$ interaction of lone electron pairs (LEP)[16], and the $n-\pi$ interaction of LEP with an unsaturated fragment of the molecule[17-20]. The possibility of investigating by the PES method the steric structures of conjugated molecules[16-21], the steric hindrance to conjugation[17-20], and conformational equilibria[16,21] is of considerable interest. The PES method has been used in a number of studies to investigate reactivity[22-25].

The information obtained by the PES method is extensive and varied. The threshold value of the ionisation current yields the adiabatic potential IP_m^a, which is defined as the difference between the energies of the molecules and the ion in the zero-point vibrational state. The vertical ionisation potentials IP_m^v may be determined from the maximum change in the ionisation current, which corresponds to the most probable ionisation transition.

The interpretation of the experimental data obtained by the PES method is simplest and most convenient in terms of the approximation of Koopmans' theorem[26,30], according to which the values of IP_m^v are equal to the energies (with the opposite sign) of the corresponding molecular orbital:

$$IP_m^v = -\varepsilon_m. \qquad (1)$$

In terms of the approximation of Koopmans' theorem, the ionisation potential $IP(\psi_m)$ may be regarded as the energy of the ionisation of an electron from the occupied orbital (ψ_m). In comparing the experimental values of IP_m^v with the calculated orbital energies $(-\epsilon_m)$, one also uses relations of the type

$$IP_m^v = a + b(-\varepsilon_m), \qquad (2)$$

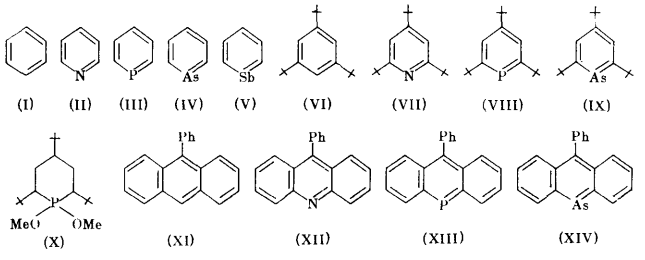
which have come to be referred to as the weakened form of Koopmans' theorem [31,32].

However, the empirical methods for the interpretation of PES data, based on the definite characteristic nature of the properties of the bands in the spectrum, are no less valuable. Thus the LEP of oxygen, sulphur, and halogen atoms contribute specific narrow bands to the photoelectronic spectra, while the delocalisation of the LEP, particularly their involvement in the $n-\pi$ interaction, leads to a broadening of the bands and a change in their shape [5]. When the LEP electrons of nitrogen [33] and phosphorus [34] are dislodged, broad bands are obtained (the difference between IP_1^v and IP_1^a amounts in this case to approximately 0.5 eV), which is associated both with the involvement of the LEP of these atoms in bonding and with the change in the geometry of the ion on ionisation. The upper π orbitals of conjugated systems give rise to narrow bands with a resolved vibrational structure [5]. The intensity of the bands depends both on the nature of the atom where the corresponding orbital is predominantly localised and on the contribution to the latter by s and p electrons [35].

In the interpretation of PES data, relations governing series of related compounds are used, the spectra of the test compound and its perfluoro-analogue are compared [36], and account is taken of the spin–orbital and Jahn–Teller band splitting [37,39] as well as the dependence of the band intensity on the degree of degeneracy of the orbitals [37] and the energy of the ionising radiation [38]. The above procedures make it possible in many instances to interpret fairly unambiguously the photoelectron spectrum and to determine the energy of the orbitals and the nature of their interaction.

II. λ^3-PHOSPHORINS

The photoelectron spectra of λ^3-phosphorin and its derivatives



have been obtained and interpreted by Schäfer's [40-45] and Heilbronner's [46] groups. The disposition of the molecular orbitals in λ^3-phosphorin was established by comparison with *ab initio* calculations [46] and with calculations by the method of complete neglect of differential overlapping (CNDO/2) [40,41] and was confirmed by ionisation potential data for series of related compounds [43-45] (Fig. 1 and Table 1).

Table 1. The vertical ionisation potentials of λ^3-phosphorins and their interpretation.

Compound	IP^v, eV					Refs.
λ^3-Phosphorin	9.2 $3b_1(\pi)$	9.8 $1a_2(\pi)$	10.0 $13a_1(\sigma, n)$	11.5 $8b_1(\sigma)$	12.1 $2b_1(\pi)$	46
2,4,6-Tri-t-butylphosphorin	8.0 π_1	8.6 π_2	8.6 n	10.0		40
9-Phenyl-10-phosphanthracene	7.25	8.65	9.00	9.30	9.90	42
2-Phenyl-1-phosphanaphthalene	7.65 π_1	8.40 π_2	8.9 Ph, n	9.4	9.8 π_3	44
2-Phenylnapthalene	7.75 π_1	8.30 π_2	8.95 Ph	9.3	9.95 π_3	44
10-Phenyl-9-phosphanthracene	7.60 π_1	8.15 π_2	8.85 π_3	9.25 Ph, n	9.80 π_4	45
10-Phenylanthracene	7.65 $\pi_1(b_1)$	8.05 $\pi_2(a_2)$	8.90 $\pi_3(a_2)$	9.20 Ph	9.75 $\pi_4(b_1)$	45
2,4,6-Tri-t-butyl-1,1-dimethoxyphosphorin	6.7 $\pi_1(b_1)$	8.4 $\pi_2(a_2)$				43
1,1-Dibenzyl-2-phenyl-1-phosphanaphthalene	6.0 π_1	7.90 π_2	8.8 Ph, B_Z, π_3	9.4		44

When a heteroatom is introduced into the benzene molecule, the upper degenerate benzene orbital $1e_{1g}(\pi)$ splits into two orbitals of the type $b_1(\pi)$ and $a_2(\pi)$, in conformity with the C_{2v} symmetry group of the substituted molecule. Since the atomic coefficient of the $a_2(\pi)$ orbital is zero at the site of substitution, the orbital should be little affected by the influence of the substituent (Fig. 2). In contrast to $a_2(\pi)$, the $b_1(\pi)$ orbital has no node at the site of substitution and its energy must depend significantly on the nature of the substituent. In terms of the approximation of the Hückel method, the change in the energy of the $b_1(\pi)$ orbital is determined by the product of the square of the atomic coefficient at the site of substitution and the Coulomb integral for the heteroatom $\Delta\alpha_X$:

$$\Delta\varepsilon(b_1(\pi)) = [C_{b_1(\pi),x}]^2 \Delta\alpha_x. \qquad (3)$$

The absence of a charge on the phosphorus atom in the $a_2(\pi)$ orbital also follows from the electron density map for the $b_1(\pi)$ and $a_2(\pi)$ orbitals of the λ^3-phosphorin molecule [47].

In the pyridine molecule, the energy of the $a_2(\pi)$ orbital is higher than that of the $b_1(\pi)$ orbital, because the nitrogen atom is more electronegative than carbon and stabilises the $b_1(\pi)$ orbital. In contrast to the pyridine molecule, in λ^3-phosphorin and in heterocyclic arsenic(IV) and antimony(V) compounds, the $b_1(\pi)$ orbital lies above the $a_2(\pi)$ orbital (Fig. 1). The reversal of the sequence of π orbitals in λ^3-phosphorin in relation to pyridine constitutes the main problem in the interpretation of the photoelectron spectra of these compounds [40-46]. The reversal of the orbitals has been comprehensively investigated and demonstrated in several ways. The reversal of the sequence of π orbitals can be demonstrated by quantum-chemical calculations of λ^3-phosphorin [46]. We shall also examine empirical methods for the elucidation of the reversal of levels and the conclusions concerning the electronic structure of the

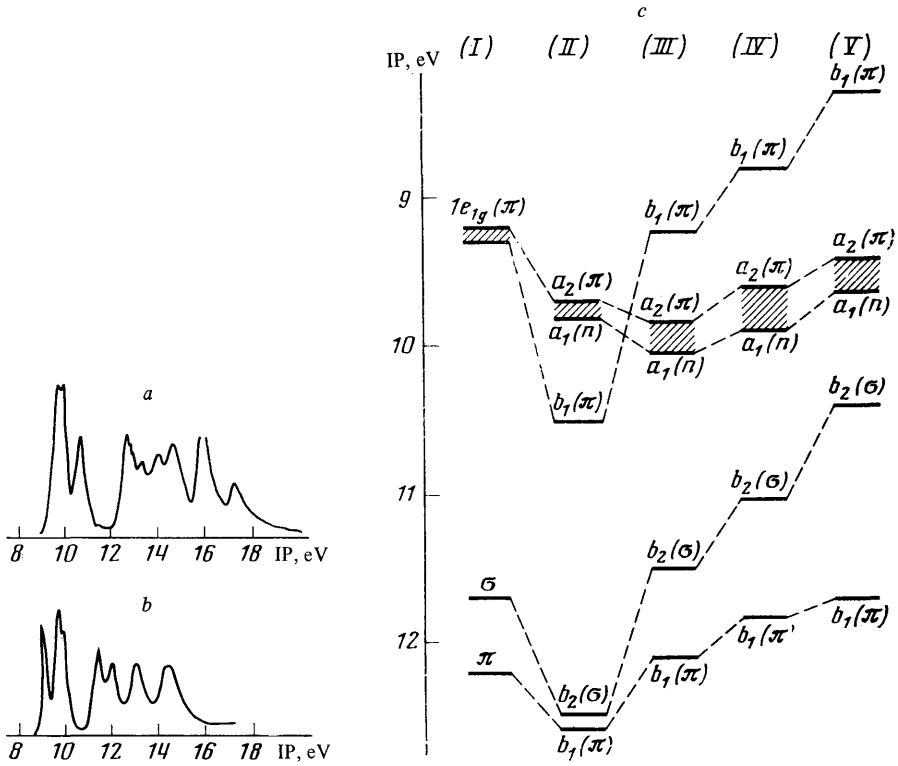


Figure 1. Photoelectron spectra: *a*) pyridine (II); *b*) λ^3-phosphorin (III); *c*) correlation energy level diagram for compounds (I)–(V).[46]

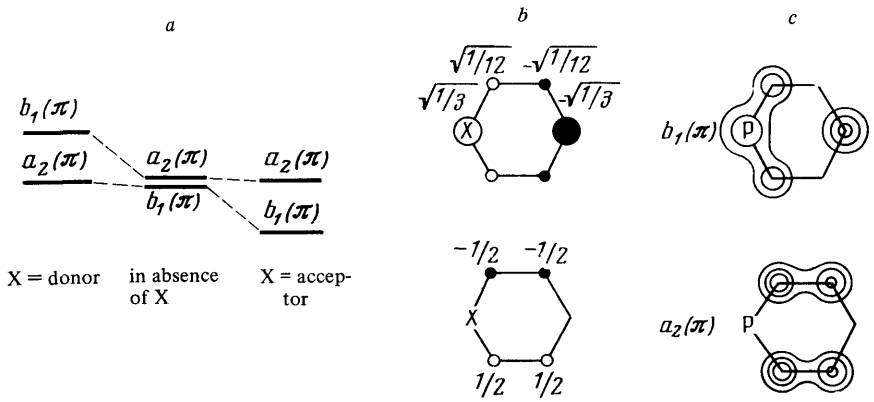


Figure 2. The influence of the substituents X on the relative positions of the $a_2(\pi)$ and $b_1(\pi)$ orbitals (*a*), a schematic representation of the atomic coefficients of these orbitals (*b*), and electron density maps for the $a_2(\pi)$ and $b_1(\pi)$ orbitals of λ^3-phosphorin (*c*).[47]

λ^3-phosphorin molecule which follow from this reversal. In the series of compounds (I)–(V), the ionisation potentials of the $b_1(\pi)$ orbitals are correlated with the ionisation potentials IP(X) of the atoms X:

X	N	C	P	As	Sb
IP(X), eV	14.53	11.26	11.0	9.81	8.64

when the reversal of orbitals is postulated[46]. In the derivation of the relation

$$IP^v[b, (\pi)] = 5.24 \text{ eV} + 0.362 \text{ IP(X)}, r = 0.9998 \quad (4)$$

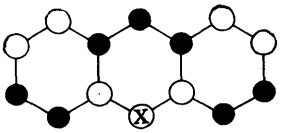
$IP_3^V[b_1(\pi)]$ was used for pyridine and $IP_1^V[b_1(\pi)]$ was used for the remaining compounds. The ionisation energy of the second occupied π orbital of the $b_1(\pi)$ type is also correlated with IP(X):

$$IP^v[b, (\pi)] = 10.25 \text{ eV} + 0.163 \text{ IP(X)}. \quad (5)$$

In compounds (I)–(V), the potentials $IP[b_1(\pi)]$ vary less than IP(X), because the atomic coefficient $C_{b_1,X}$ of this orbital is significantly less than unity at the site of substitution. $(C_{m,X})^2 = 1/3$ is obtained for the upper $b_1(\pi)$ orbital and $(C_{m,X})^2 = 1/6$ is obtained for the second orbital of the $b_1(\pi)$ type[46]. In conformity with Eqn. (3), these squares of the atomic coefficients should determine the slopes of the linear relations between $IP[b_1(\pi)]$ and IP(X); the empirical slopes of the straight lines, described by Eqns. (4) and (5), are indeed very close to 1/3 and 1/6.

The nitrogen atom, which exhibits electron-accepting properties, stabilises the $b_1(\pi)$ orbital in pyridine [IP(N) = 14.53 eV, IP(C) = 11.26 eV]. In contrast to this, the phosphorus, arsenic, and antimony atoms destabilise the $b_1(\pi)$ component of the $1e_{1g}$ orbital of the benzene molecule, showing at the same time electron-donating properties. However, whereas the $b_1(\pi)$ orbitals in λ^3-phosphorin are destabilised compared with the corresponding benzene orbitals, the $a_2(\pi)$ orbital is additionally stabilised. It has been noted[46] that, according to *ab initio* calculations, a shift of electron density away from the phosphorus atom is observed in λ_3-phosphorin.

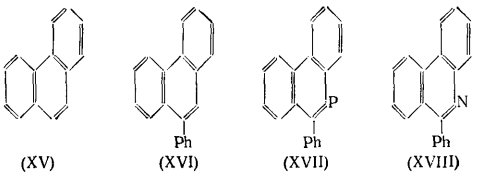
The inversion of the sequence of orbitals in compounds (I)–(V) and (VI)–(VIII) was also observed when the $IP^V[b_1(\pi)]$ of these compounds were compared with the IP_1 of the anthracene hetero-derivatives[42]. The problem of the degeneracy of the orbitals and of their disposition after the removal of degeneracy, which is crucial for benzene derivatives, is altogether absent for anthracene and its derivatives. In anthracene, the upper occupied $b_{2g}(\pi)$ orbital is not degenerate, its energy is much higher than that of the subsequent orbitals, and it has no node at any of the atoms:



$b_{2g}(\pi)$

Like the orbital of the $b_1(\pi)$ type, this orbital should be subject to the inductive influence of the heteroatom X (Fig. 3).

The photoelectron spectra of compounds (XI)–(XIV) show a separate band of the π type, which unambiguously determines the value of IP_1^V. The inversion of the orbital sequence follows from the fact that the IP_1^V of compounds (XI)–(XIV) are correlated with the values of $IP^V[b_1(\pi)]$ of compounds (I)–(V) and (VI)–(IX), selected taking into account the inversion. Since the atomic coefficient of the $b_{2g}(\pi)$ orbital at the site of substitution is smaller than the corresponding coefficient of the $b_1(\pi)$ orbital in benzene, the range of variation of IP_1^V in compounds (XI)–(XIV) is also significantly narrower than in compounds (I)–(V) and (VI)–(IX) (Fig. 3). Like the correlation equations (4) and (5), these data also indicate the applicability of Eqn. (3) to the description of the dependence of the energy of the orbital without a node at the site of substitution on the electronegativity of the heterosubstituent.



(XV) (XVI) (XVII) (XVIII)

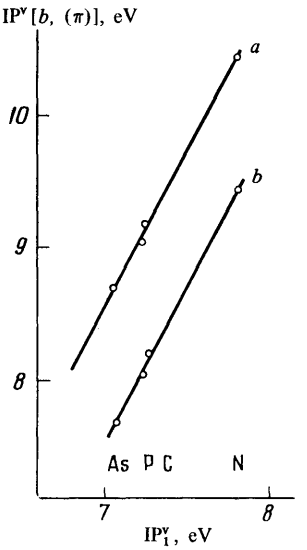


Figure 3. Relation between $IP^V[b_1(\pi)]$ and IP_1^V of compounds (I)–(IV) and (XI)–(XIV) (*a*) and compounds (VI)–(IX) and (XI)–(XIV) (*b*).[42]

In their discussion of the photoelectron spectra of compounds (XV)–(XVIII), Schäfer et al.[45] concluded that the electronic influences of the phosphorus atom and the sp^2-hybridised carbon atom are identical, because, in contrast to the nitrogen-containing hetero-derivative (XVIII), the upper ionisation potentials of 9-phenyl-λ^3-phosphaphenanthrene (XVII) and 9-phenylphenanthrene (XVI) are extremely close (Fig. 4). The changes in the ionisation potentials of 2-phenylnaphthalene are just as small when the carbon atom in the 1-position is substituted by phosphorus[4] (Table 1). However the initial compounds (benzene and λ^3-phosphorin) have different photoelectron spectra; the substitution of a carbon atom by phosphorus removes the degeneracy and shifts the ionisation potentials of some of the orbitals, although to a much smaller extent than does substitution by a nitrogen atom (Fig. 4). The very significant changes in the ionisation potentials for the π orbitals of 9-phenylphenanthrene and 2-phenylnaphthalene

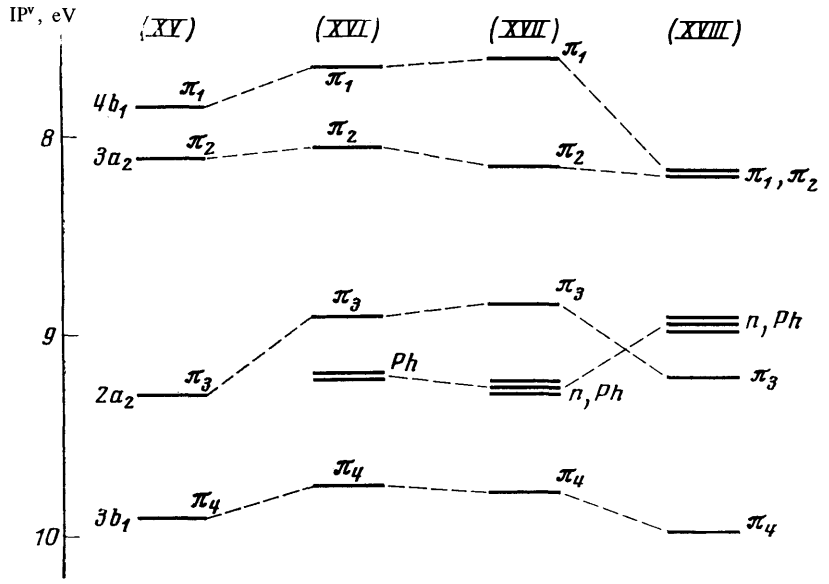


Figure 4. Correlation diagram for the ionisation potentials of compounds (XV)–(XVIII).[45]

on substitution of a carbon atom by phosphorus can be readily understood: the π orbitals in the 9-phenylphenanthrene molecule are significantly delocalised, the atomic coefficients of the individual orbitals at the site of substitution are small and, according to Eqn. (3), the corresponding changes in the orbital energies and ionisation potentials should be insignificant.

In the discussion of the photoelectron spectrum of λ^3-phosphorin, the problem of the role of *d* orbitals was raised. On the basis of the populations of the *d* orbitals calculated by the CNDO/2 method, Schäfer and coworkers[40,41] postulated that the additional stabilisation of the $a_2(\pi)$ level as a result of the interaction with the vacant $a_2(d_{xy})$ orbital, plays a definite role in the inversion of the $b_1(\pi)$ and $a_2(\pi)$ levels. However, the excellent correlation between IP$^V[b_1(\pi)]$ and the ionisation potentials IP(X) of the heteroatoms shows that the changes in IP$^V[b_1(\pi)]$ of λ^3-phosphorin are determined solely by the electron-donating properties of phosphorus. Furthermore, *ab initio* calculations have shown[45] that the calculated sequence of $b_1(\pi)$ and $a_2(\pi)$ orbitals in λ^3-phosphorin is independent of the inclusion of *d* orbitals in the treatment. Nevertheless, if one considers only the inductive influence of the phosphorus atom, leading to the destabilisation of the $b_1(\pi)$ orbital, it is very difficult to understand the cause of the appreciable stabilisation of the $a_2(\pi)$ orbital.

We shall consider the ionisation potentials IP(n) of the LEP of phosphorus in the photoelectron spectrum of λ^3-phosphorin and its derivatives. In the range 9.5–10 eV, the spectrum of λ^3-phosphorin has two overlapping bands (Fig. 1). Since the first has a sharper peak than the second, the authors[46] suggest that IP$_2^V$ = 9.8 eV corresponds to the $a_2(\pi)$ orbital and IP$_3^V(n)$ = 10.0 eV corresponds to the $a_1(\sigma,n)$ orbital of the lone pair. IP$^V(n)$ is 9.25 eV for 9-phenyl-λ^3-phosphaphenanthrene[45], while IP$^V(n)$ of 1,3,5-tri-t-butyl-λ^3-phosphorin is reduced to 8.6 eV.[43] It is of interest that the ionisation potentials of the $a_2(\pi)$ and $a_1(\sigma,n)$ orbitals of all the compounds in the series (II)–(VI) (Fig. 1) are similar and vary in parallel, while in the photoelectron spectra the corresponding bands are poorly resolved.

In contrast to λ^3-phosphorin, the electronic structures of λ^5-phosphorins have been investigated by the PES method to a lesser extent. The first ionisation potential of 2,4,6-tri-t-butyl-1,1-dimethoxy-λ^5-phosphorin is reduced to 6.7 eV,[43] while that of 1,1-dibenzyl-2-phenylphosphanaphthalene is only 6.0 eV.[44] The cause of such considerable destabilisation has still not been explained. It has been noted[44] that the phosphorus atom is involved in conjugation in λ^5-phosphorins.

III. COMPOUNDS OF THREE-COORDINATED PHOSPHORUS

The photoelectron spectra of compounds of three-coordinated phosphorus have been obtained by various groups of investigators[34,48–69]. In many cases, the first ionisation potential is attributed to the removal of an electron from the LEP of phosphorus. In a series of compounds investigated, this quantity varies over a wide range—from 12.29 eV for PF_3 to 7.88 eV for Ph_3P.[52,61] The dependence of the ionisation energy of the LEP on the charge of the phosphorus atom[7] and on the sum of the constants σ_I^{ph}[64] has been noted; the empirical ionisation potentials have been compared with the calculated orbital energies[61,70–72]. The adiabatic ionisation potentials IP^a have been published for a much smaller number of compounds than have the vertical potentials IP^V. We may note that the adiabatic potential has been used[70,71] in a comparison with the results of *ab initio* calculations for PH_3 and the vertical potential has been used for other compounds. The same error has been made also in a review[7]. A handbook[73] also quotes the adiabatic potentials for some compounds and the vertical potentials for others.

The difference between the values of IP$_1^V$ and IP$_1^a$ characterises the change in the geometry of the ion compared with the isolated molecule[34,49]. The differences IP$_1^V$–IP$_1^a$ for phosphine, methylphosphine, trimethylphosphine, and phosphorus trifluoride molecules are 0.64, 0.58, 0.59,

and 0.70 eV respectively[34,52,62]. In the case of chloroalkylchlorophosphines, the differences are 0.47 eV for $PCl(CH_2Cl)_2$ and 0.59 eV for $PCl_2(CH_2Cl)$.[58]

The PES method has been used[34,49] to estimate quantitatively the geometrical parameters of the ions derived from the PH_3 and PF_3 molecules. The irregularity of the vibrational levels and the appreciable broadening of the first peak indicate a somewhat pyramidal structure of the PH_3^+ ion. The PF_3^+ ion has a planar structure, because the distances between its vibrational peaks are equal. Analysis of the vibrational structures of the photoelectron spectra enabled Maier and Turner[34] and Potts and Price[49] to determine the angle between the X–H bond and the axis of rotation for a number of hydrides. In the PH_3^+ ion, the angle is approximately 87°[40] and the barrier to inversion amounts to 0.07 eV.[34]

The reciprocal relation between the photoelectron spectra and the steric structures of the trimethyl compounds (Me_3X) of Group V elements has been examined[63]. The atomic ionisation potentials of the central atom X decrease on passing from nitrogen to antimony, varying in exactly the same way as the ionisation potentials of the corresponding heterocyclic compounds (I)–(VI). In contrast to these quantities, the first ionisation potentials of the compounds Me_3X do not vary in parallel with the ionisation potentials of the atoms X. The same may be said also of the hydrides H_3X. When the heteroatom X is altered, a decrease of IP_1^V is not observed in these series of compounds (Table 2).

The anomalous constancy of the IP_1^V is associated with the decrease of the C–X–C valence angle in the series of compounds Me_3X. The C–X–C angle is 180° in trimethylamine, 99° in trimethylphosphine, and 96° in trimethylstibine. The decrease of the valence angle leads to an increase of the amount of *s* character of the LEP of the atom X on passing from nitrogen to antimony, which increases its ionisation potential. Thus the decrease of the intrinsic ionisation potential of the *p* orbital of the atom X is prevented by the increase of the amount of *s* character of the LEP, which leads to an almost constant value of the first ionisation potential.

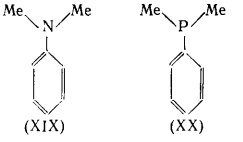
We may note that the next band in the photoelectron spectra of compounds of the type Me_3X is associated with ionisation from a degenerate orbital of the *e* type, which in contrast to LEP is largely localised at the methyl groups, and should therefore be insensitive to changes in the valence angle. The ionisation potential of this orbital $IP^V(e)$ decreases correspondingly on passing from Me_3N to Me_3Sb (Table 2), in parallel with the ionisation potential of the atom X.

Table 2. The ionisation potentials (eV) of Group V elements and their trimethyl[63] and triphenyl[61] derivatives.

Me_3X	IP(X)	IP_1^V (LEP)	IP_2^V	IP_3^V	Ph_3X	IP_1^V (LEP)
Me_3N	14.53	8.50 (a_1)	12.3 (a_2)	12.75 (e)	Ph_3N	10.27*
Me_3P	11.0	8.60 (a_1)	11.34 (e)	(13.7)**	Ph_3P	7.88
Me_3As	9.81	8.65 (a_1)	10.70 (e)	(13.6)	Ph_3As	7.95
Me_3Sb	8.64	8.48 (a_1)	10.3 (e)	(13.3)	Ph_3Sb	8.18

*$IP_1^V(\pi) = 6.99$ eV; $IP^V(LEP) = 10.27$ eV.
**The values in brackets have been determined approximately.

We shall now examine the manifestation in the photoelectron spectra of the interaction of the LEP of phosphorus with a conjugated system. The spectra of phenylphosphines have been published by several groups of investigators[53,59–61,64], the authors conclusions about the electronic structures of phenylphosphines differing somewhat.



(XIX) (XX)

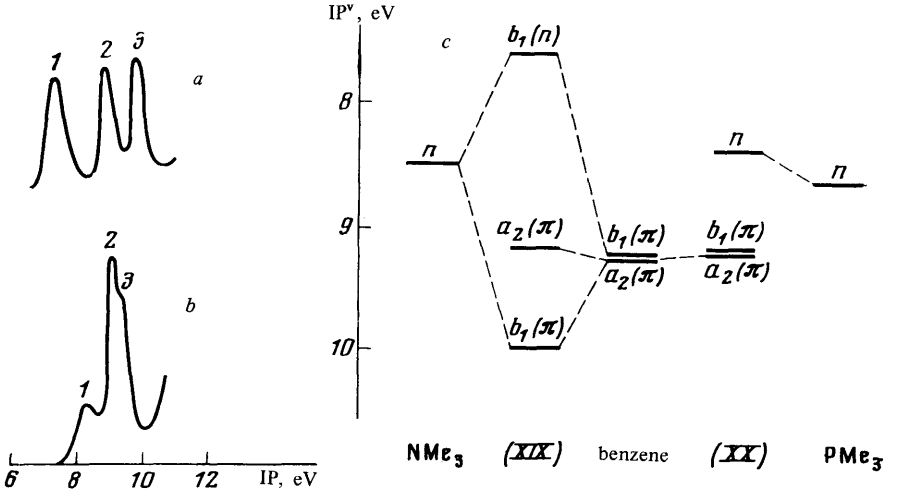


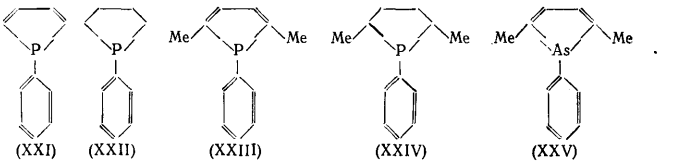
Figure 5. Photoelectron spectra and their interpretation[59]: *a*) *NN*-dimethylaniline (**XIX**); *b*) dimethylphosphine (**XX**).

Whereas the spectrum of *NN*-dimethylaniline has three bands of equal intensity in the region of low potentials at 7.6, 9.2, and 10.0 eV, the spectrum of dimethylphenylphosphine shows not three but two bands of different intensities, at 8.45 and 9.2 eV (Fig. 5). The second, more intense band with a maximum at 9.2 eV is not resolved into two components. The spectra of the two related molecules have been interpreted[59] in terms of the $n-\pi$ approximation, i.e. the upper occupied orbitals are represented as a combination of n and π orbitals of the heteroatom and the benzene ring. The vertical ionisation potential of the LEP of the Me_3N molecule is 8.5 eV, while the ionisation potential of the degenerate $1e_{1g}$ π orbital of benzene is 9.24 eV. As a result of the interaction with the LEP of the nitrogen atom, the degenerate $1e_{1g}$ level of benzene in dimethylaniline is split into two. The orbital of type $a_2(\pi)$, having a node at the site of substitution, does not interact with the LEP of nitrogen and its energy does not change. In contrast to it, the $b_1(\pi)$ orbital, which does not have a node at the site of substitution, interacts vigorously with the n orbital of nitrogen, forming two orbitals with b_1 symmetry. The upper occupied $b_1(n-\pi)$ orbital receives a preferential contribution from the LEP of the nitrogen atom, while the $b_1(\pi + n)$ orbital is mainly of the π type. The significant change in the energies of the resultant orbitals indicates an appreciable $n-\pi$ interaction in the dimethylaniline molecule (Fig. 5).

In contrast to *NN*-dimethylaniline, the energy of the highest occupied orbital in dimethylphenylphosphine is higher by only 0.15 eV compared with Me_3P, while the band corresponding to the degenerate benzene orbital is not split into two (Fig. 5). Hence the authors[59] conclude that there are two virtually unconnected fragments in dimethylphenylphosphine: the system of the benzene ring and the LEP of phosphorus. Accordingly IP_1 was assigned to the ionisation of the LEP of phosphorus and IP_2 to the unsplit $a_2(\pi)$ and $b_1(\pi)$ orbitals of the phenyl substituent.

We may note that the photoelectron spectra of substituted benzenes PhX, where X is a substituent containing nitrogen[17,19], sulphur[67], oxygen[17,74,75], halogens[4,75], a double bond[20], or the phenyl group[76], have been fairly well investigated. It has been shown that the splitting of the $1e_{1g}$ level depends both on the nature of the heteroatom and on the dihedral angle between the interacting fragments—the π-electron system of the benzene ring, and the n or π orbital of the substituent. Later data were obtained demonstrating the orthogonality of the plane of the benzene ring and the LEP of phosphorus[77], but no stereochemical conclusions were reached in the study by Schäfer and Schweig[59].

The next communication by the same workers[60] contains, in their view, direct proof of the non-aromatic nature of phospholes and arsoles.



(XXI) (XXII) (XXIII) (XXIV) (XXV)

The spectrum of compound (XXI) has two bands (Fig. 6), each of which refers to ionisation from two orbitals of similar energies. The appearance of the first band is interpreted as a result of ionisation from the $a_2(\pi)$ orbital of the cyclopentadiene system and the LEP of phosphorus and the second has been assigned to the π orbitals of the phenyl substituent. Owing to hyperconjugation, the methyl substituent in the phosphole fragment increases the energy of the $a_2(\pi)$ cyclopentadiene orbital, because the energies of this orbital and the LEP of phosphorus become different. In the spectrum of the hydrogenated derivative (XXII), the component of the first band corresponding to the ionisation from the $a_2(\pi)$ cyclopentadiene orbital is absent, since the

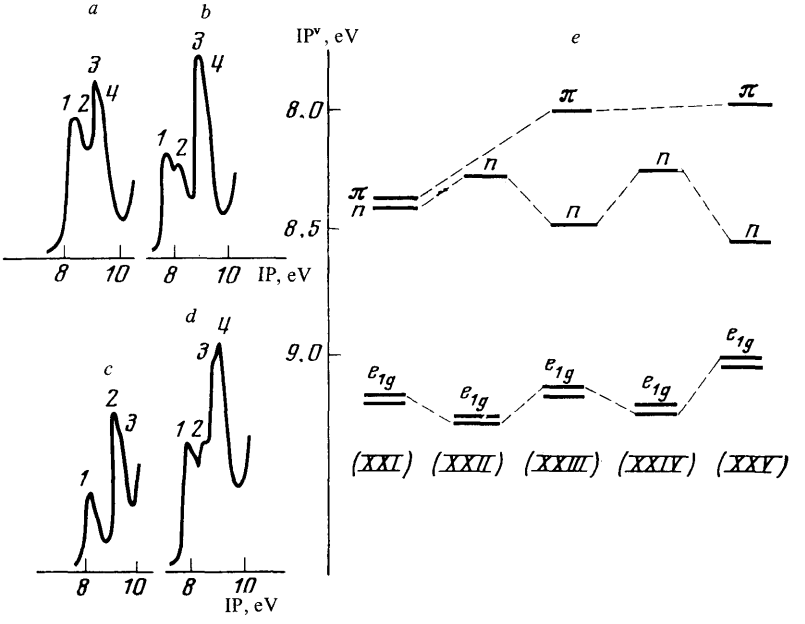


Figure 6. Photoelectron spectra of heterocyclic compounds: *a*) (XXI); *b*) (XXIII); *c*) (XXII); *d*) (XXV); *e*) correlation diagram for the ionisation potentials in the (XXI)–(XXV) series[60].

first band of this compound has reduced intensity and refers solely to the LEP of phosphorus. The above facts show that in the ground state the molecule of phosphole (XXI) has three non-conjugated fragments—the π-electron system of the phenyl substituent, the LEP of the phosphorus atom, and the localised diene system. The authors[59] speak of the non-aromatic nature of phosphole precisely in this sense. According to a calculation by the CNDO/2 method[72], the C_4H_4NH molecule is planar, while the angle between the plane of the cyclopentadiene fragment and the P–H bond in the C_4H_4PH molecule is approximately 90°.

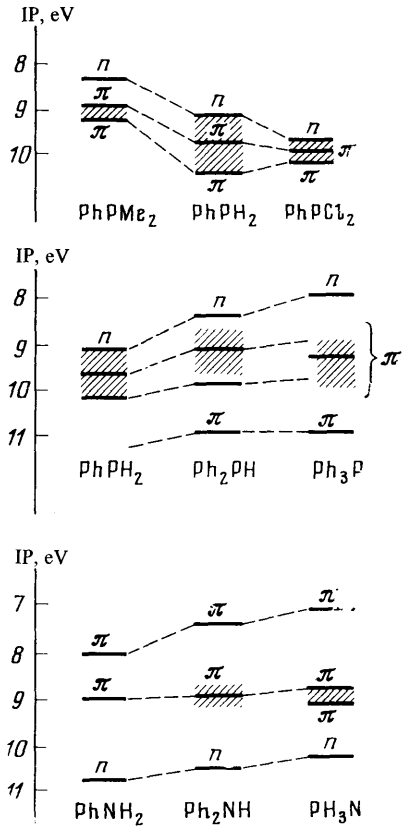


Figure 7. Vertical ionisation potentials and band widths (shaded regions) in the photoelectron spectra of phenyl derivatives of Group V elements[61].

Betteridge et al.[53] note the absence of the splitting of the π level of the phenyl substituent in dichlorophenylphosphine. They suggest that the first band, with a maximum at 9.7 eV, corresponds to ionisation from three orbitals—two orbitals of the π level of the phenyl group and the LEP of phosphorus. However, they do not indicate the absence of interaction between the LEP and the π-electron system of the phenyl substituent. They postulate that, firstly, the PCl_2 substituent is an electron acceptor compared with hydrogen and, secondly, that a substituent of this kind does not lead to the splitting of the upper level of benzene in other instances either. However, the authors do not quote an example confirming this conclusion, while it is known that electron-accepting substituents such as Cl,[4] F,[75] NO_2,[78] and CN [79] cause a very significant splitting of this level. Quantitative analysis of the spectra of $PhPCl_2$ on benzene enabled Betteridge et al. to conclude that the first band in the photoelectron spectrum of $PhPCl_2$ is compound. They also quote[53] the photoelectron spectrum of triphenylphosphine, but do not discuss this spectrum or the corresponding band assignments.

Debies and Rabalais[61] quote the photoelectron spectra of a large series of phenyl derivatives of Group V elements (Fig. 7). Thus the first ionisation potentials of phenylphosphines have been interpreted[53,59,60] as the energy required to dislodge an electron from the LEP of phosphorus. This result has been additionally confirmed by comparing the spectra of phenylphosphine and aniline obtained using two radiation sources. Compared with the experiments involving the use of the He(I) line, the use of the radiation of the He(II) line reduces the intensity of the signals due to the electrons dislodged from the 3*s* and 3*p* orbitals of phosphorus to a greater extent than the signal of the electrons dislodged from the 2*s* and 2*p* orbitals of carbon[36]. The employment of He(II) radiation in the case of phenylphosphine reduces the intensity of the shoulder on the band in the region of low energies relative to the central part of the band, which confirms the validity of the assignment of the shoulder to ionisation from the phosphorus *n* orbital and of the central band to the ionisation of the phenyl π electrons. The fact that the intensity of the shoulder does not diminish quite as much as in other phosphorus compounds[61] shows that this orbital is delocalised to an even greater extent.

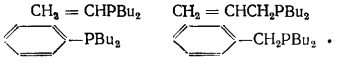
On successive substitution of the hydrogen atoms in phosphine (as well as in arsine and stibine), the intensity of the band corresponding to the phosphorus *n* orbital remains unchanged, while the intensities of the subsequent bands, corresponding to ionisation from the π orbitals, increase owing to the increase of the number of π electrons. This finding shows that, as in phenylphosphine, in diphenyl- and triphenyl-phosphines the first ionisation potential refers to the phosphorus *n* orbital. On the other hand, in phenylamines there is a change in intensity not in this first band but in one of the subsequent bands in the region of higher ionisation energies.

In contrast to studies[53,59,60] where it was concluded that there is no splitting of the $a_2(\pi)$ and $b_1(\pi)$ components of the $1e_{1g}$ level of benzene in phenylphosphines, the large combined bands were resolved by Debies and Rabalais[61] into their components and the IP_V corresponding to the individual $a_2(\pi)$ and $b_1(\pi)$ orbitals were thus determined (Fig. 7). The splitting obtained in this way is small (0.66 eV in phenylphosphine, while the value in aniline is 1.1 eV) and can probably be partly caused by the inductive influence of the PH_2 group. Debies and Rabalais suggest that, in contrast to the stabilisation of the *n* orbital in phenylamines, the destabilisation of the *n* orbital in phenyl-substituted phosphorus, arsenic, and antimony compounds is a consequence of the shift of electron density from the phenyl substituent to the phosphorus, arsenic, or antimony atom via the d_π–p_π mechanism. However, not only in phenylphosphine but also in *NN*-dimethylaniline[59], in phenylhydrazones[74], and in iodobenzene[4], i.e. in all cases where the energy of the initial *n* orbital is higher than that of the π orbital, the upper destabilised orbital is predominantly of the *n* type when the orbitals interact (Fig. 8). In contrast to *NN*-dimethylaniline, in aniline itself the energy of

the ground n orbital is below the energy of the $b_1(\pi)$ orbital and the upper orbital is predominantly of the π type.

According to Debies and Rabalais[61], the anomalous sequence of the IP_1^V of the compounds Ph_3X (Sb > As > P) compared with the electronegativity series and the atomic ionisation potentials (Sb < As < P) is also a consequence of the involvement of d orbitals in the interaction. It is suggested that the inversion of the sequence of ionisation potentials is caused by the reduced involvement of d orbitals in the interaction when the size of the central atom increases, this being accompanied by a decrease of charge transfer to the central atom and an increase of the ionisation potential of the molecule. However, in the series of trimethyl compounds Me_3X (Table 2), the same anomalous sequence of potentials, caused by the increase of the contribution of the s orbital to the upper occupied n orbital with increased size of the heteroatom and decreased the C–X–C valence angle, is observed.

Additional evidence showing that the interaction between the LEP of phosphorus and the π-electron system is weak was provided by a study of compounds with the methylene group[64]:



According to calculation by the CNDO/2 method, the most favoured conformation of the above compounds is one where the LEP of phosphorus lies in the plane of the π-electron system and does not interact with it[64]. The photoelectron spectra of the compounds indicate an appreciable interaction between the π orbitals and the P–C bond.

The interaction of the LEP of the phosphorus atom and that of the neighbouring atom X linked to it was also investigated by the PES method. Analysis of the n–n interaction is one of the most important achievements of the PES method. The dependence of the n–n interaction on stereochemical factors has been investigated in a series of compounds with N–N, O–O, and S–S bonds[16,80,82]. The two equivalent LEP n and n' orbitals interact through space or via a bond and form two semi-localised orbitals (Fig. 8):

$$n^+ = \frac{1}{\sqrt{2}}(n + n') \text{ and } n^- = \frac{1}{\sqrt{2}}(n - n').$$

The difference between $IP(n^+)$ and $IP(n^-)$ characterises the efficiency of the interaction and depends on the disposition of the LEP in space[18,80–82].

The photoelectron spectrum of the compound F_2PPF_2 has been obtained[52]. The first ionisation potential of 9.64 eV was assigned to a symmetrical combination (n^+) of the LEP of the phosphorus atoms, while the second ionisation potential (12.45 eV) was assigned to their antisymmetrical combination (n^-). The observed difference between ionisation potentials $IP_2^V - IP_1^V = 2.81$ eV indicates an extremely effective interaction between the LEP. The energy of the individual LEP in the F_2PPF_2 molecule, given by $\frac{1}{2}(IP_1^V + IP_2^V) = 11.04$ eV, proved to be close to the first ionisation potential of F_2PH (11.0 eV), which confirms the above interpretation of the first two ionisation potentials of F_2PPF_2.

A lower degree of n–n interaction of the LEP of phosphorus in the compounds Me_2PPMe_2 and $(CF_3)_2PP(CF_3)_2$ was later reported[56,57]; the manifestation of conformational isomerism was observed in the photoelectron spectra. In the region of low ionisation energies, the photoelectron spectra of these compounds contain three peaks. Two of these, IP_1^V and IP_3^V, correspond to the n^+ and n^- combinations of the LEP of the *trans*-conformer. The third low-intensity IP_2^V peak indicates the presence of a certain amount of the *gauche*-conformer, for which there is no n–n splitting (Table 3). According to the authors, the fact that the average IP^V (LEP) of the *trans*-conformer is somewhat smaller than the corresponding value for the *gauche*-conformer is associated with the slight destabilisation arising when the *trans*-oriented LEP interact. However, we may note that contradictory results, obtained in a study of the conformational isomerism by the PES method[21], have also been published.

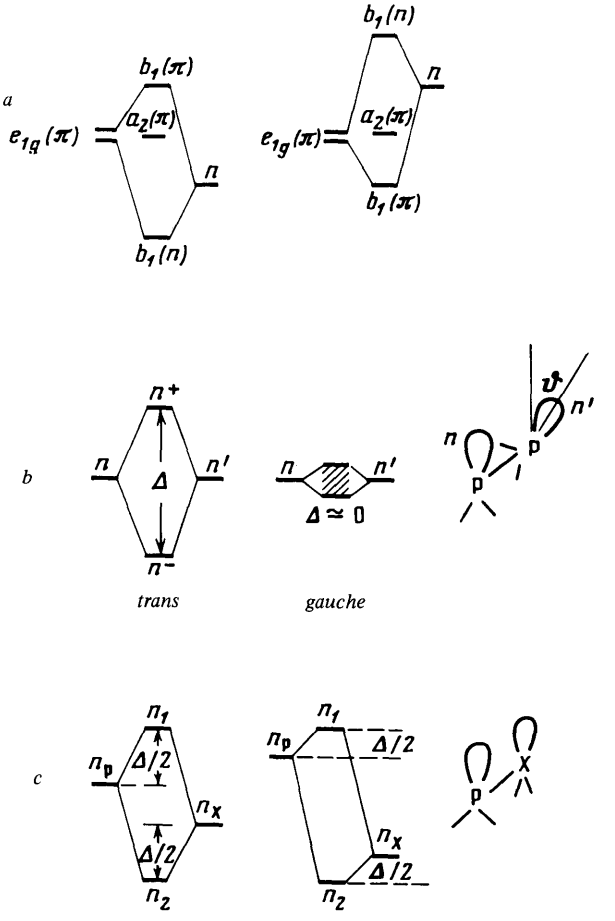


Figure 8. Dependence of the n–π (*a*) and n–n interactions on the relative energies of the initial orbitals: b) for equivalent n orbitals; c) for non-equivalent n orbitals.

For a number of molecules such as those of $(CF_3P)_m$, containing different numbers of phosphorus atoms, the average potentials are correlated with the induction constant (as a consequence of the interaction of the LEP of the phosphorus atoms). This finding indicates an insignificant role of the d_π–p_π interaction in the above molecules[57].

The study of the n–n interaction of non-equivalent LEP by the PES method is much more complicated. In this case, the difference between ionisation potentials $IP(n^+)$ – $IP(n^-)$, referring to the n orbitals, does not in any way

characterise the extent of the $n-n$ interaction (Fig. 8). The difference $IP(n^+) - IP(n^-)$ is determined by the difference between the LEP energies before interaction and by the $n-n$ splitting, both quantities being unknown. However, in the Me_2PCl molecule one of the chlorine LEP (of the a'' type) is not involved in the interaction with the phosphorus LEP and thus plays the role of an internal standard, which makes it possible to estimate the extent of the $n-n$ interaction between the chlorine LEP (a' type) and the phosphorus LEP.[65] The possibility of the interaction between the LEP of the phosphorus and chlorine atoms in the PF_2Cl molecule was also assumed by Bassett and Lloyd[52], but they postulated that the LEP of the individual atoms in the F_2POPF_2 molecule do not interact with one another.

Table 3. The vertical ionisation potentials (eV) and the percentage contents of the conformers[57].

Compound	Content of conformers, %	IP^V(LEP)	IP^V(P-P or As-As)	IP^V(P-P or As-C)
gauche-Me_4P_2	16	8.79	10.33	11.22; 11.83
trans-Me_4P_2	84	7.88; 9.54	10.33	11.22; 11.83
gauche-Me_4As_2	12	8.85	9.82	10.60; 11.21
trans-Me_4As_2	88	7.91; 9.50	9.82	10.60; 11.21
gauche-$(CF_3)_4P_2$	10	11.57	13.09	13.49
trans-$(CF_3)_4P$	90	10.71; 12.11	13.09	13.49
trans-$(CF_3)_4As_2$	100	10.39; 11.94	12.07	12.58

Dewar and coworkers[56] compared the photoelectron spectra of a number of compounds with the P–N bond: $(Me_2N)_mPF_{5-m}$ and $(Me_2N)_mPF_{3-m}$. The spectra were interpreted in terms of the n approximation. In all cases, IP_1 was assigned to ionisation from the LEP of nitrogen (Table 4). If the interpretation of IP^V given below is adopted, it is found that the substitution of the ethyl group at the nitrogen atom by a methyl group has a considerable influence on the phosphorus LEP[65]:

Compound	LEP, N	LEP, P
Et_2NPF_2	9.45	10.25
Me_2NPF_2	9.60	10.50

It is suggested that this is caused by a change in the valence and torsional angles. The hypothesis of the $n-n$ interaction, described by the difference $IP(n,P)-IP(n,N)$, has been used to explain the change in the torsional energy barrier to rotation about the P–N bond, which is anomalous in relation to the degree of steric hindrance[66].

Compounds of three-coordinated phosphorus PX_3, containing equivalent groups X = halogen, OR, NR_2, etc., are convenient for the investigation of the relation between PES data and the stereochemistry of the molecule. If the molecular symmetry is C_2 or C_{3v}, then the upper occupied orbitals should include degenerate orbitals of the e type. The bands corresponding to these orbitals in the photoelectron spectrum should have approximately doubled intensities or should undergo spin-orbital or Jahn–Teller splitting[55,77]. When the molecule has a lower symmetry, the e levels are absent under these conditions.

$P(Hal)_3$ molecules have the C_{3v} symmetry and their photoelectron spectra have been interpreted in terms of ideas of this group of workers[53,55]. The first ionisation potentials are associated with ionisation from the non-bonded a_1, a_2, and e orbitals. The a_1 orbital is preferentially localised at the phosphorus atom, while the a_2 and e orbitals arise as a result of the interaction of the three equivalent LEP of the halogens. The band corresponding to the e orbital in the spectra of PBr_3 and PI_3 undergoes spin–orbital splitting[54].

Table 4. The vertical ionisation potentials (eV) of the LEP of nitrogen [N(2p)] and phosphorus [P(3p)].

Compound	N (2p)	P (3p)
Me_2NPF_4	10.35	—
$(Me_2N)_2PF_3$	8.84; 9.95	—
$(Me_2N)_3PF_2$	8.04; 9.03; 9.31	—
$(Me_2N)PF_2$	9.58	10.48
$(Me_2N)_2PF$	8.18; 9.14	10.40
$(Me_2N)_3P$	7.61; 7.89; 8.86	9.98

Table 5. The ionisation potentials of $P(OMe)_3$, the band intensities I (arbitrary units), and band assignments[53].

IP^V_m, eV	I	Orbital symmetry	Localisation region
9.0	1	a	LEP, P
10.6	2	e	LEP, O
11.1	4	$a+e+a$	LEP, O + C–O, σ
12.4	2	e	P—O, σ
13.0	1	a	P—O, σ

In their interpretation of the photoelectron spectrum of $P(OMe)_3$, Betteridge et al. used data for the ionisation potentials of methanol[53]: 11.0 eV (LEP, O); 12.7 eV (C–O, σ); 15.0 eV (CH_3). The C_{3v} symmetry was adopted for the $P(OMe)_3$ molecule and the molecular orbitals were represented by a combination of the LEP of phosphorus, the three equivalent LEP of oxygen, the C–O σ bonds, etc. Accordingly a band corresponding to the ionisation of the LEP of phosphorus, two bands with the 1 : 2 intensity ratio associated with the a and e orbitals produced as a result of the $n-n$ interaction of the three LEP of the oxygen atoms (n_O), two bands with an intensity ratio of 1 : 2 associated with the a and e orbitals of the three C–O σ bonds, etc. should accordingly be expected in the $P(OMe)_3$ spectrum. The interpretation of the photoelectron spectrum of $P(OMe)_3$ obtained in this way is illustrated in Table 5. We believe that the interpretation of this spectrum (Fig. 9) corresponds to the C_3 and not the C_{3v} symmetry type. For the C_3 symmetry, where the LEP of oxygen does not undergo π-type overlapping, the degenerate $e(n_O)$ orbital should in fact be the second from above.

The mechanisms of the $n-n$ interactions of the LEP of phosphorus (n_P), oxygen (n_O), and nitrogen (n_N) atoms are examined in Figs. 9 and 10. In the case of σ-type overlapping[83], where the LEP (n_X) axes of the X_3 atoms are located in the X_3 plane, the energy of the semilocalised $e(n_X)$ orbital is also smaller than that of the $a(n_X)$ orbital. For the π-type overlapping of the LEP (n_X), the opposite relative positions of the $a(n_X)$ and $e(n_X)$ levels are obtained. In contrast to the π approximation, the n approximation, i.e. consideration of n electrons independently of the σ framework, is less justified[13]. The overlap integrals of the n_X orbitals in the compounds PX_3 are small and $n-\sigma$ mixing can therefore exceed the degree of the $n-n$ interaction, leading to a different sequence of orbitals in the molecule.

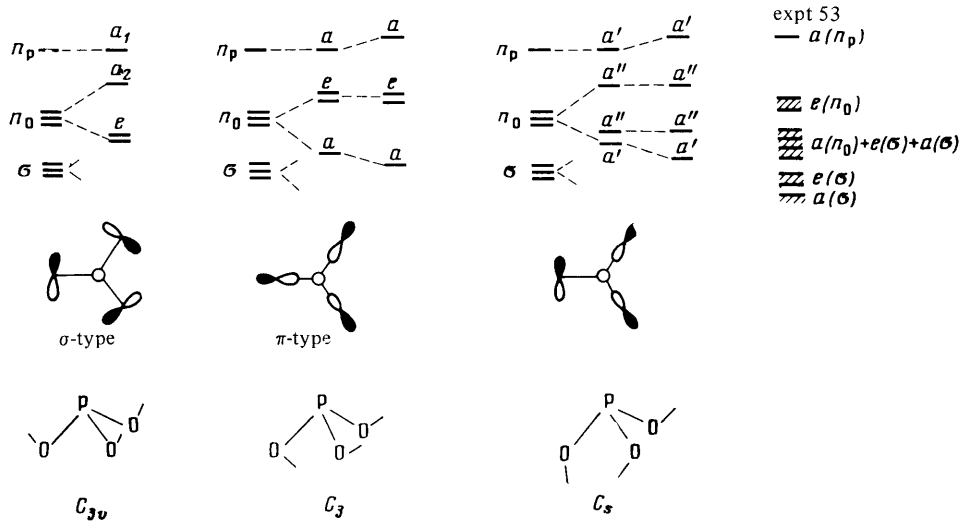


Figure 9. Schematic illustration of the n–n interaction of the LEP of the oxygen (n_O) and phosphorus (n_P) atoms.

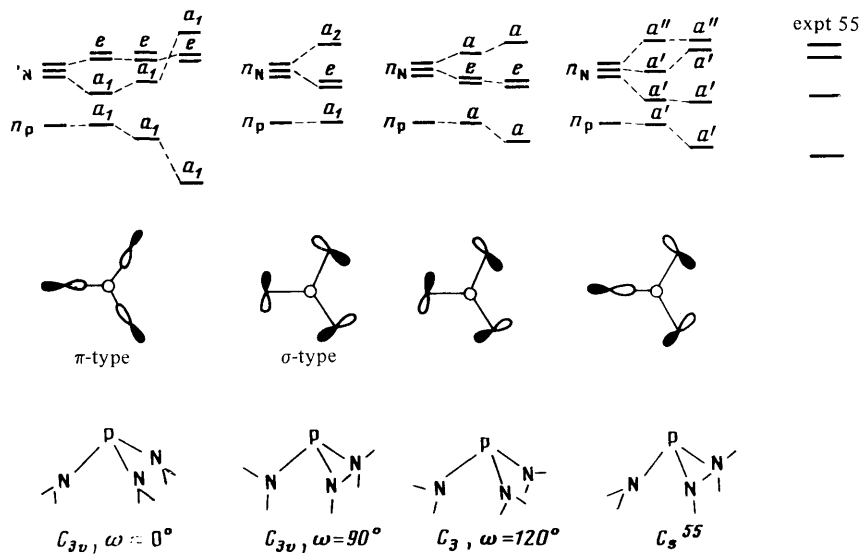


Figure 10. Schematic illustration of the n–n interaction of the LEP of the nitrogen (n_N) and phosphorus (n_P) atoms.

Fig. 11 illustrates a correlation diagram for the $P(OH)_3$ and $P(OMe)_3$ orbital energies calculated by the CNDO/2 method[84]; the geometrical parameters were taken from Naumov and coworkers[85]. The orbital sequence obtained differs from the sequence which may be predicted in terms of the n approximation (Fig. 9). The energies of the orbitals of the model compound $P(OH)_3$ reproduce in the same way the photoelectron spectrum of $P(OMe)_3$ for structures with C_3 and C_S symmetries (Fig. 11). The intense bands with maxima at 10.6 and 11.1 eV are extremely broad and may be due to a superposition of close overlapping bands. We believe that calculations on $P(OMe)_3$ assuming the C_S symmetry gives the best agreement with experiment. In the case of the C_3 symmetry, the two neighbouring e-type orbitals might have given rise to individual bands. The total energies of the structures with the C_3 and C_S symmetries of the model compound $P(OH)_3$ proved to be similar, but the $P(OMe)_3$ structure with the C_S symmetry is energetically more satisfactory. Naumov and coworkers[85] also quote qualitative evidence in support of the C_S symmetry in $P(OMe)_3$ based on electron diffraction.

According to Cowley et al.,[55] the C_S symmetry of the $P(NMe_2)_3$ molecule obtained by Vilkov[86] conflicts with the photoelectron spectrum of the molecule. Experimental data show that the upper occupied orbitals have similar energies, while in the case of the C_3 symmetry the degenerate orbital is the second highest (Fig. 10). Cowley et al.[55] proposed the C_S symmetry for $P(NMe_2)_3$. In this

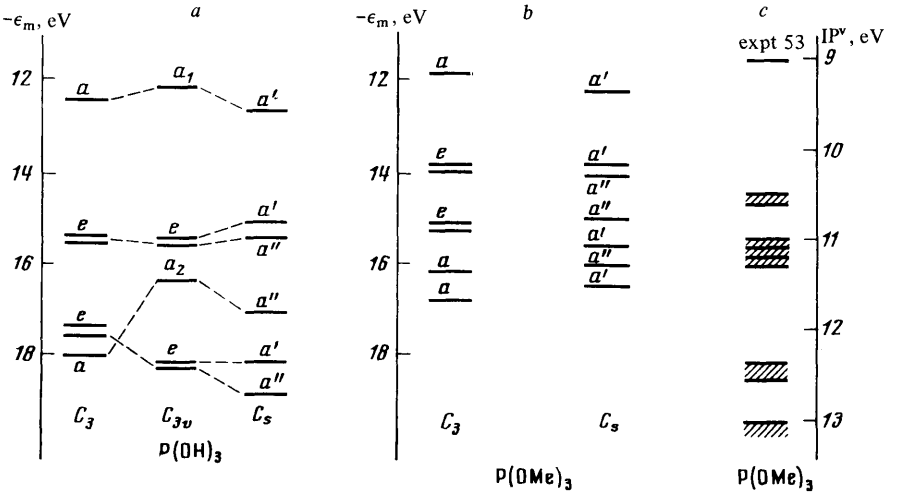


Figure 11. Theoretical dependence of the energies of P(OH)$_3$ (*a*) and P(OMe)$_3$ (*b*) on the steric structure of the molecules (CNDO/2 method) together with experimental data[53] (*c*).

case IP_1 and IP_3 correspond to the n^+ and n^- combinations of the nitrogen LEP involved in σ-type overlapping, while IP_2 and IP_4 correspond to the same combinations of the phosphorus and nitrogen LEP (Fig. 10). It is suggested that the structure with the C_s symmetry is stabilised owing to the smaller degree of the Coulombic repulsion of the LEP.

The compound B(NMe$_2$)$_3$, which has a similar structure, had been investigated previously by Bock and Fuss[87]. In conformity with the π-type overlapping, the second band corresponds to an *e*-type orbital (C_3 symmetry). The smaller difference $IP_2^V - IP_1^V$ for B(NMe$_2$)$_3$ (1.62 eV) compared with its cyclic analogue (2.2 eV) was explained by the propeller rotation of the amino-group about the B–N bond ($\omega = 33°$). In contrast to aminoborines, the $n-\sigma$ mixing and the Jahn–Teller splitting of the *e* orbital were resorted to in order to explain the photoelectron spectra of cyclohexane hetero-derivatives on the basis of C_3 symmetry[82].

IV. COMPOUNDS OF FOUR-COORDINATED PHOSPHORUS

The most systematic studies on the photoelectron spectra of compounds in the series WPXYZ for W = O or S have been carried out by Vovna, Vilesov, and coworkers[58, 88–93]. The spectra of individual compounds were also obtained by other workers[37,53,71] and Bock's group studied the interaction between X_3P and BH_3 as well as the photoelectron spectra of ylids[68,94]. The PES[58] method has been used to analyse the intramolecular interactions in compounds of four-coordinated phosphorus. Calculation by the CNDO/2 method[95] reproduces satisfactorily the changes in the ionisation potentials of the compounds WPXYZ. Thus the values of IP_1^V for the compounds OPF$_3$ and OPMe$_3$ are 13.52 and 9.76 eV,[68] while the calculated values ($-\epsilon_1$) are 18.84 and 14.18 eV respectively.

The form of the photoelectron spectra of the compounds WPXYZ resembles that of the spectra of the corresponding tervalent phosphorus compounds PXYZ, but there are also significant differences (Fig. 12). The formation of the WP bonds leads to the disappearance of the band due to the ionisation of the phosphorus LEP (n_P) orbital. The band corresponding to the ionisation of the four p_π electrons of W as well as a band (in the region of high ionisation energies) corresponding to the σ_{PW} orbital of the newly formed W–P bond appear in the WPXYZ spectra. The remainder of the spectrum, characterising the ionisation of electrons from orbitals localised preferentially at the X, Y, and Z atoms, remains unchanged, being displaced towards higher ionisation energies in conformity with the electronegativity of the WP group. The first ionisation potential characterises the energy of the binding of the p_π electrons of the W atom and the series of subsequent potentials is related to the ionisation of the LEP of the substituents. Thus, according to Zverev et al.,[58] the formation of the $\dot{O}PCl(OEt)_2$, $OPCl(\dot{O}Et)_2$, and $OP\dot{C}l(OEt)_2$ radical-cations from the OPCl(OEt)$_2$ molecule requires energies of 10.96, 11.50, and 12.28 eV respectively. In certain compounds with a P–N bond, the nitrogen atom exhibits the greatest electron-donating capacity and the first ionisation potential is determined by the nitrogen LEP. Comparison of the energies of the n_P, $p_{\pi,W}$, and σ_{PW} orbitals characterises the degree of charge transfer and the amount of double-bond character of the WP linkage. The stabilisation of the σ_{PW} orbital compared with the n_P orbital indicates charge transfer from the P atom to W, while the energy of the $p_{\pi,W}$ orbital may be a measure of the reverse transfer and the amount of double bond character[68].

The band appearing on formation of the W=P bond in the region of low ionisation energies and determining the values of IP_1 of a large number of compounds (Table 6) is fairly characteristic of this class of compounds. In the spectra of the compounds WPX_3, belonging to the C_{3v} or C_3 symmetry group, this band arises on ionisation from a degenerate *e*-type orbital localised preferentially on the $p_\pi(p_x, p_y)$ orbitals of the W atom. The broad shape of the band contour indicates the involvement of the $p_{\pi,W}$ orbital in the bonding between W and P atoms. It has been suggested on the basis of a comparison with calculations[37, 52,71,96] that this orbital is involved in $p_{\pi,W} - p_{\pi,P}$ and $p_{\pi,W} - d_{\pi,P}$ interactions. The fact that in the spectra of molecules of the type WPXYZ the band is not split into two

components is regarded as evidence for the insignificant delocalisation of the orbital over the XYZ group of atoms.

Following Zverev et al.,[58] we shall examine a series of additional factors characterising the $e(p_\pi)$ orbital of the W=P bond. In the compounds WPX_3 (X = Cl, Br, or OEt), the LEP of the substituents X_3 give rise to two semilocalised orbitals $a_2(n_X)$ and $e(n_X)$. A change in the inductive influence of the W atom should cause the same shifts of the energies of these orbitals, while conjugation, leading to mixing of the $e(n_X)$ orbital with other e-type orbitals, can alter the difference between the energies of the $a_2(n_X)$ and $e(n_X)$ orbitals. Experimental data (Table 7) show that in the PCl_3 molecule this difference is smaller (0.3 eV) than in the $OPCl_3$ (0.63 eV) and $SPCl_3$ (0.59 eV) molecules, i.e. in these molecules the $e(n_X)$ orbital interacts more effectively with e-type orbitals: the occupied $e(p_\pi)$ orbital or the vacant $e(d_\pi)$ orbital. However the interaction between the $e(n_X)$ and $e(p_\pi)$ orbitals cannot be significant, because the difference between the energies of the $a_2(n_X)$ and $e(n_X)$ orbitals remains constant for the compounds OPX_3 and SPX_3, despite the significant difference between the energies of the $e(p_\pi,S)$ and $e(p_\pi,O)$ orbitals[58].

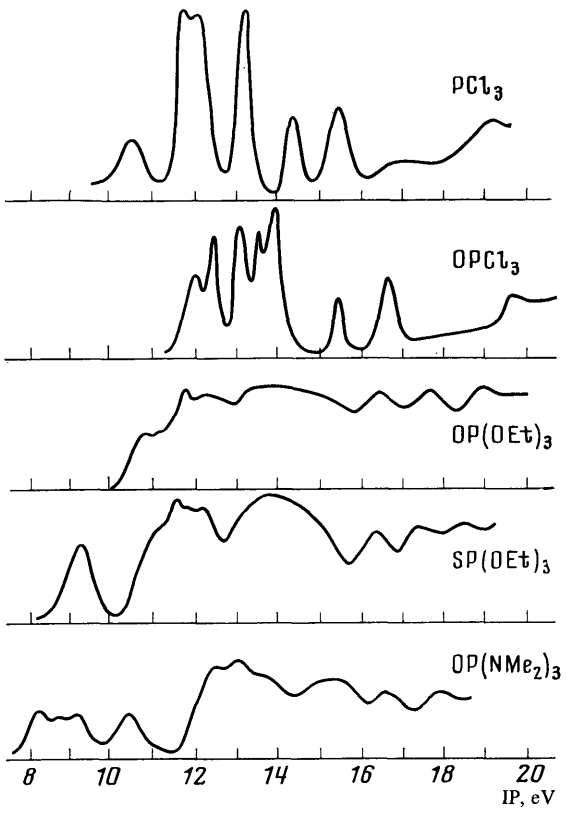


Figure 12. Photoelectron spectra of certain compounds of the type WPXYZ[58,90,91].

In contrast to the WPX_3 molecules under consideration, a number of data for the compound $OP(NMe_2)_3$ indicate the mixing of the p_π,O orbital with the nitrogen n orbitals. This mixing of the orbitals greatly reduces the ionisation potentials of the n orbitals and increases the ionisation energy of the p_π,O orbital. The dependence of the ionisation potentials corresponding to ionisation from the p_π,W orbital on the constants σ^* and σ^{Ph} has been examined[58]. The nitrogen-containing molecules of the phosphoryl series constitute a special group; owing to mixing with the nitrogen n orbitals, the ionisation potentials corresponding to ionisation from the p_π,O orbital in such compounds are larger than in the case where account is taken of the inductive influence alone.

Table 6. The vertical ionisation potentials of the compounds SPXYZ and OPXYZ referring to the p_π orbital of the W=P bond[37,58,68,89-91].

XYZ	IP_1^V	XYZ	IP_m^V
SPXYZ *		OPXYZ *	
Cl_3	10.15	Cl_3	11.91
$Cl_2(OEt)$	9.81	Cl_2OEt	11.46
$Cl(OEt)_2$	9.41	$Cl(OEt)_2$	10.96
$(OEt)_3$	8.96	$(OEt)_3$	10.54
Cl_2Ph	9.47	$(OMe)_3$	10.81
Cl_2NMe_2	9.35	$Cl(OPr)_2$	10.89
$Cl(NMe_2)_2$	8.75	Cl_2OPh	11.40
$(NMe_2)_3$	8.05	$Cl(CH_2Cl)_2$	10.75
Br_3	9.89	$(OEt)(CH_2Cl)_2$	10.19
$Cl(CH_2Cl)_2$	9.54	Cl_2Me	11.49
$(OBu)_3$	8.28	Br_3	11.07
Et_2OPr	8.55	$Cl_2(NMe_2)$	11.28
Me_3	8.53	$Cl(NMe_2)_2$	10.90
		$(NMe_2)_3$	10.44
		$(OEt)_2NHNH_2$	10.90
		$(Me)_3$	9.76
		F_3	13.52

*The values of IP_1^V are quoted for SPXYZ.
**IP_3^V for XYZ = Cl_2OPh, $Cl(NMe_2)_2$, or $(OEt)_2NHNH_2$, IP_2^V for XYZ = Cl_2NMe_2, IP_4^V for XYZ = $(NMe_2)_3$, and IP_1^V in the remaining cases.

Table 7. Energies of ionisation from a- and e-type orbitals and the differences between them (eV).

Orbital	$SP(OEt)_3$	$OP(OEt)_3$	$SPCl_3$	$OPCl_3$	Orbital	PCl_3
$1e$	8.96	10.54	10.15	11.91	$1a_1$	10.53
$1a_2$	10.73	10.96	12.03	12.37	$1a_2$	11.73
$2e$	11.43	11.56	12.62	13.00	$1e$	12.03
$2e-1a_2$	0.70	0.60	0.59	0.63	$1e-1a_2$	0.30
$2e-1e$	2.47	1.02	2.49	1.15		

Direct experimental evidence for the delocalisation of the p_π,O orbital in the direction of the atoms of the substituents is provided by the photoelectron spectrum of $OPBr_3$.[37] In this compound, spin–orbital splitting of the highest occupied e orbital by the atoms of the substituents is observed, which indicates its delocalisation over the Br_3 atoms.

Comparison of the values of $-\Delta G^\circ$ for the formation of the complexes XYZPO...I_2 [97] with the ionisation potentials of the compounds XYZPO confirms the interpretation of the $OP(NMe_2)_3$ spectrum and the scheme describing the mixing of the p_π,O and n_N orbitals (Fig. 13). $-\Delta G^\circ$ for the compound $OP(NMe_2)_3$ is correlated with a potential intermediate between IP_4^V and IP_3^V. IP_4^V refers to the p_π,O orbital, but is increased owing to the $p_\pi - n_N$ interaction. A similar effect is manifested also for $OPCl(NMe_2)_2$. In contrast to a series of compounds of the type XYZPO, in

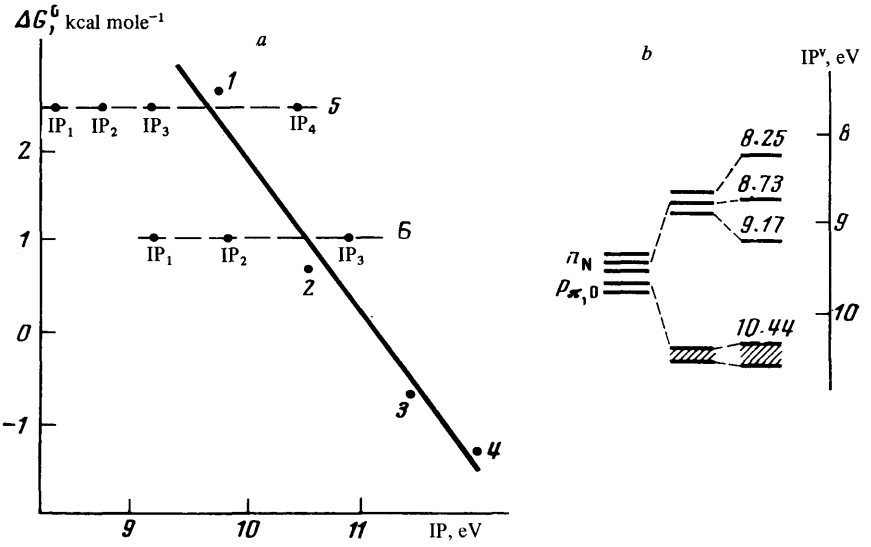


Figure 13. Dependence of $-\Delta G^\circ$ for the formation of complexes of the compounds XYZPO with I_2 (Paetzold and Niendorf[97]) on IP_I^V for different compounds (*a*) [1) Me_3PO; 2) $(EtO)_3PO$; 3) $(EtO)Cl_2PO$; 4) Cl_3PO; 5) $(Me_2N)_3PO$; 6) $(Me_2N)_2ClPO$ (the values of several IP_m^V are indicated for compounds *5* and *6*)] and schematic illustration of the interaction between the orbitals of compound *5* (*b*).

the compounds SPXYZ investigated, the energy of the $p\pi$,S orbitals is characterised in all cases by the potential IP_I^V. Hence the following relation has been found to hold[92]:

$$-\Delta G^0 = -2.7\ IP_I^V + 25.7.$$

We may note that in the series of dihexylphenylphosphines[69] a linear relation has been observed, as in the compounds WPXYZ, between pK_a characterising the basicity in solution and IP(LEP) of phosphorus:

$$pK_a = -4.8\ IP_n^V + 42.2.$$

Table 8. The ionisation potentials of the LEP of the XYZ ligands in the compounds OPXYZ and SPXYZ and their assignments.

XYZ	IP(LEP), eV		Assignment
OPXYZ		SPXYZ	
$Cl(OEt)_2$	12.28	12.00	LEP, Cl
$Cl(CH_2Cl)_2$	12.69	12.33	LEP, Cl
$Cl_m(OEt)_{3-m}$	12.13	11.83	LEP_{av}, XYZ
Br_3	11.70	11.18	LEP_{av}, Br_3
$Cl_2(OEt)$	11.89	11.59	LEP, O
$Cl_2(NMe_2)$	9.87	9.92	LEP, N

Comparison of the ionisation potentials for the LEP of the substituents X, Y, and Z (both the individual values of IP_m^V and the values averaged with respect to the *n* orbitals) makes it possible to consider the problem of the effective electronegativity of the WP groups. The ionisation potentials IP_{n_X} of the LEP (X = Cl, Br, or OEt) form the sequence $IP_{n_X}(OP) > IP_{n_X}(SP) > IP_{n_X}(P)$, i.e. the effective electronegativity increases in the sequence OP > SP > P. The OP group thus exhibits the greatest electron-accepting influence (Table 8).

Table 9. Certain ionisation potentials and NQR frequencies[99] of the compounds OPXYZ and SPXYZ.

XYZ	OPXYZ	SPXYZ	Assignment of potential
	IP^V, eV		
Cl_2OEt	11.89	11.59	LEP, O
$Cl(OEt)_2$	11.65	11.37	LEP, O
$(OEt)_3$	11.36	11.20	LEP_{av}, O
$Cl_2N(Me)_2$	9.87	9.92	LEP, N
$Cl(NMe_2)_2$	9.31	9.62	LEP, N
$(NMe_2)_3$	8.72	9.13	LEP_{av}, N
	ν_{P-Cl}, MHz		
Cl_3	28.950	29.735	
Cl_2Ph	26.635	27.840	

The above sequence is infringed by the ionisation potentials of the orbitals localised preferentially at the LEP of nitrogen, which form the sequence SP > OP > P (Tables 8 and 9). For example, in the compounds $WP(NMe_2)_3$ the average ionisation potentials of the nitrogen LEP form the sequence 9.13 (SP) > 8.72 (OP) > 8.12 (P). The additional decrease (compared with the inductive influence of the OP group) of the potentials of the nitrogen LEP is due to the resonance interaction of the $p\pi$,O orbitals and the nitrogen *n* orbitals. It is of interest that comparison of both ^{35}Cl and ^{14}N NQR frequencies yields the same sequence of the effective electronegativities of the groups: SP > OP > P.[98]

Comparison of the ionisation potentials of the LEP of the substituents also makes it possible to examine the role of the W atom in the transmission of the electronic effect of substituents via the WP group (Tables 8 and 9). In the

compounds OPXYZ, the range of variation of the ionisation potentials of the LEP of the OEt or NMe_2 group is greater after substitution by chlorine atoms than in the SPXYZ series. In view of its more pronounced electron-accepting properties and greater amount of double bond character, the OP group is apparently a better transmitter of the influence of the X atom in the X–PO–Y_2 molecule on the ionisation potentials of the LEP of the Y_2 group. The corresponding effects are also shown when the NQR frequencies are compared (Table 9) and in kinetic measurements[100].

We shall next consider the photoelectron spectra and the structures of individual compounds. The compound $SPCl_2Ph$ gives rise to a well resolved spectrum, which makes it possible to determine 14 ionisation potentials[89]. The first ionisation potential (9.47 eV) is due to the $3p_\pi$ electrons of sulphur and the next (9.93 eV) was assigned to the unsplit ($a_2 + b_1$) π orbitals of the phenyl group. Thus the addition of the phenyl group to a four-coordinated phosphorus atom, like the addition to a three-coordinated phosphorus atom, does not split the upper π level of benzene. According to Vovna et al.,[89] the absence of splitting shows that the $SPCl_2$ substituent exhibits only an inductive influence. Vilkov's electron diffraction data[101] showed that the benzene ring in the compound $OPCl_2Ph$ lies in the plane of the OPC atoms. The mutual orthogonality of the two π-electron systems (Ph and SP) is apparently the cause of the absence of splitting.

The $OP(OMe)_3$ and $OP(OEt)_3$ spectra obtained by Vovna et al.[91] were interpreted on the assumption that the molecules have C_{3v} symmetry. The three equivalent LEP of the oxygen atom give rise to two semilocalised orbitals of the a_2 and e types. Although the photoelectron spectra of these compounds, like that of $SP(OEt)_3$,[90] are poorly resolved, it is possible to establish that the e-type orbital lies below the a_2 orbital. In terms of the n approximation, this implies σ-type overlapping of the oxygen LEP (Fig. 9).

However, according to electron diffraction data[102], the compound $OP(OMe)_3$ exists as a mixture of two conformers with C_3 symmetry. The calculated energies of the upper levels in the compounds $WP(OR)_3$, like those in $P(OMe)_3$ (Fig. 11), change little when the steric orientation of the methyl groups is varied. Furthermore, the inversion of the relative positions of the a_2- and e-type levels formed by the oxygen LEP in the compounds $P(OMe)_3$ and $OP(OMe)_3$ is striking: the e-type orbital in $P(OMe)_3$ lie above the a orbital[53], while the opposite situation obtains in $OP(OMe)_3$. It is difficult to say whether this is due to experimental error or is a consequence of molecular structure. There is no inversion in the compounds $PHal_3$ and $WPHal_3$.

The spectra of $P(NMe_2)_3$ and $OP(NMe_2)_3$ in the region of the ionisation of the nitrogen LEP contain three peaks of approximately equal intensities (Fig. 12). If the molecules had a threefold symmetry axis, one would expect the presence in the spectrum of two peaks and not three, with an intensity ratio of 1 : 2. The cause of the absence of the spectroscopic manifestation of the e level was not discussed by Vovna and coworkers[89,91], but Betteridge et al., who also obtained the photoelectron spectrum of $OP(NMe_2)_3$, put forward three hypotheses[53]. Firstly, the observed photoelectron spectrum may be a result of a superposition of several spectra, secondly the P–N σ orbitals may also have low ionisation potentials, and finally, the molecule does not have the C_{3v} symmetry. The authors themselves are inclined to accept the last hypothesis.

The compound $OP(NH_2)_3$ was investigated by X-ray diffraction[103] and it was shown that the positions of the nitrogen atoms deviate appreciably from the C_{3v} symmetry. The O–P–N valence angles differ by 10°. Such appreciable infringement of the C_{3v} symmetry may, however, be a consequence of the formation of intermolecular hydrogen bonds in the crystalline state, while in the gas phase the molecule may have a different structure. Fig. 14 presents a diagram of the $OP(NH_2)_3$ levels, calculated by the CNDO/2 method taking into account d orbitals. In all the versions, the positions of the nitrogen atoms are the same and correspond to the C_{3v} symmetry. Fig. 14 shows that even a change in the positions of two hydrogen atoms causes a significant alteration in the relative positions of the levels. The e-type orbital, localised preferentially at the nitrogen atoms should be split on reduction of symmetry to C_S into widely separated a' and a'' orbitals, in agreement with experiment. Such a marked dependence of the energies of the orbitals on the configuration of the atoms (in contrast to the data in Fig. 11) is apparently a consequence of the greater delocalisation of the nitrogen LEP compared with the oxygen LEP.

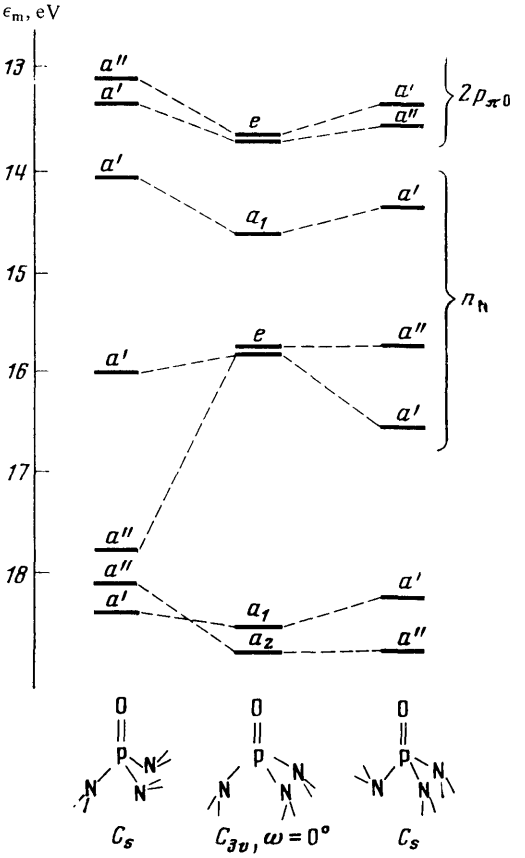


Figure 14. Theoretical dependence of the energy of the $OP(NH_2)_3$ orbitals on structure (calculation by the CNDO/2 method).

Like other phosphorus ylids, the compound $Me_3P{=}CH_2$ has a low ionisation potential, which indicates the accumulation of a large negative charge on the carbon atom of the CH_2 group, which has been confirmed by CNDO/2 calculations. The only band in the region of low ionisation energies, determining the first ionisation potential, arises in

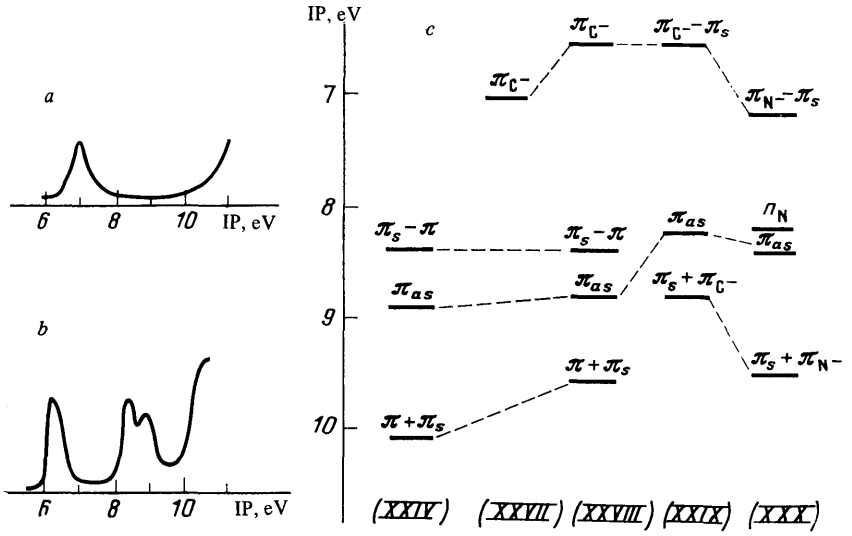


Figure 15. Photoelectron spectra: *a*) compound (XXVII); *b*) compound (XXIX); *c*) IP_m^v correlation diagram for compounds (XXVI)–(XXX).[94]

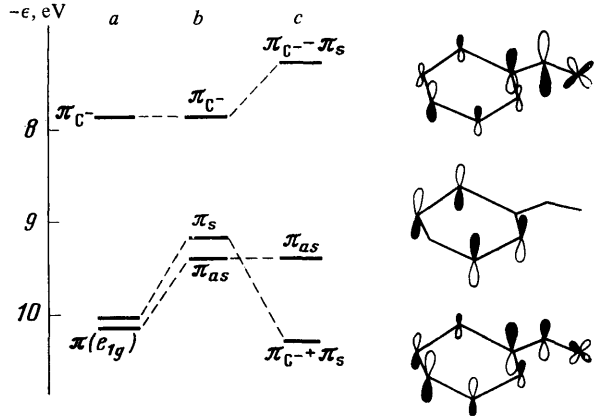
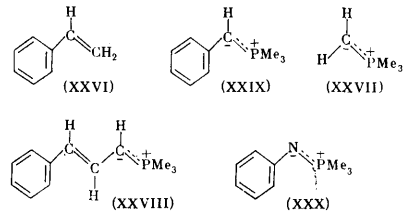


Figure 16. Analysis by the CNDO/2 method of the electronic structure of compound (XXIX); orbital energies of compounds (XXVII) and benzene (*a*) and compound (XXIX) allowing for Coulombic interaction but not for the conjugation of the ylid and phenyl fragments (*b*) and taking into account both forms of interaction (*c*).[94,104]

the $Me_3P{=}CH_2$ spectrum following ionisation from the "carbanionic" π_{C^-} orbital, which is localised preferentially at the carbon atom of the CH_2 group[94] (Fig. 15).



Two additional bands, due to ionisation from orbitals localised preferentially in the phenyl substituent, appear in the $Me_3P{=}CHPh$ spectrum. The first is the $\pi_{as}(a_2)$ benzene orbital, which does not interact with the "carbanionic" π_{C^-} orbital by virtue of symmetry, and the second characterises the energy of the mixed $\pi_S + \pi_{C^-}$ orbital, where π_S is the symmetrical $\pi(b_1)$ orbital. The first ionisation potential is determined by the energy of the $\pi_{C^-} - \pi_S$ orbital (Fig. 15). The experimentally observed splitting of the energies of the π_{as} and $\pi_S + \pi_{C^-}$ orbitals, which is particularly pronounced in $Me_3P{=}NPh$, indicates the conjugation of the "carbanionic" centre with the phenyl substituent.

It is remarkable that the energy of ionisation from the π_{as} orbital as well as from the $\pi_S + \pi_{C^-}$ orbital is smaller than the ionisation potential of benzene, which shows that not only IP_1 but also the ionisation energies corresponding to the removal of electrons from orbitals localised preferentially in the phenyl substituent decrease under the influence of the field of the negative charge of the "carbanionic" centre. CNDO/2 calculations (Fig. 16), carried out by Ostoja Starzewski et al.,[104] reveal clearly the successive influence of the field and conjugation on the energies of the upper occupied orbitals.

---o0o---

The photoelectron spectra of compounds of two-, three-, and four-coordinated phosphorus were examined above. The information obtained about the electronic structures of these molecules in the gas phase is extensive and has been interpreted fairly unambiguously; it demonstrates the fruitfulness of the application of the PES method to the chemistry of organophosphorus compounds, the centenary of the birthday of one of the founders of which, Academician A. E. Arbuzov, has been celebrated by the scientific community of the USSR.

REFERENCES

1. F.I.Vilesov, B.L.Kurbatov, and A.N.Terenin, Dokl. Akad. Nauk SSSR, 138, 797, 1329 (1961).
2. D.W.Turner and M.J.Al-Joboury, J.Chem.Phys., 37, 3007 (1962).
3. K.Siegbahn and C.Nordling, "Electron Spectroscopy" (Translated into Russian), Izd.Mir, Moscow, 1972.
4. D.W.Turner, C.Baker, A.B.Baker, and C.R.Brundle, "Molecular Photoelectron Spectroscopy", Wiley–Interscience, London, 1970.
5. A.D.Baker and D.Betteridge, "Photoelectron Spectroscopy" (Translated into Russian), Izd.Mir, Moscow, 1975.
6. H.Bock and C.G.Ramsay, Angew.Chem.Intern. Edit., 12, 734 (1973).
7. D.Betteridge and M.Thompson, J.Mol.Struct., 21, 341 (1974).
8. V.N.Nefedov, "Stroenie Molekul i Khimicheskaya Svyaz'" (Molecular Structure and the Chemical Bond), Izd.VINITI, Moscow, 1975, Vol.3.
9. V.I.Vovna and F.I.Vilesov, "Uspekhi Fotoniki" (Advances in Photonics), Izd.Leningrad.Gos.Univ., Leningrad, 1975, No.5, p.3.
10. M.Beez, G.Bierd, H.Bock, and E.Heilbronner, Helv.Chim.Acta, 56, 1028 (1973).
11. H.D.Martin and R.Schwesinger, Ber., 107, 3143 (1974).
12. R.Gilbert, E.Heilbronner, M.Hekman, and H.-D.Martin, Ber., 106, 28 (1973).
13. V.V.Zverev, M.S.El'man, L.V.Ermolaeva, and Yu.P.Kitaev, Zhur.Obshch.Khim., 44, 2272 (1974).
14. M.E.Akopyan, "Uspekhi Fotoniki" (Advances in Photonics), Izd.Leningrad.Gos.Univ., Leningrad, 1973, No.5, p.31.
15. D.G.Stretts and G.P.Ceasar, Molec.Phys., 26, 1037 (1973).
16. S.F.Nelsen, J.M.Buschak, and P.J.Hintz, J.Amer. Chem.Soc., 95, 2011, 2013 (1973).
17. J.P.Maier and D.W.Turner, J.Chem.Soc., Faraday Trans., II, 69, 521 (1973).
18. V.V.Zverev, V.I.Vovna, M.S.El'man, Yu.P.Kitaev, and F.I.Vilesov, Dokl.Akad.Nauk SSSR, 213, 1117, 1319 (1973).
19. S.A.Cowling and R.A.W.Johnstone, J.Electron. Spectr., 2, 161 (1973).
20. J.P.Maier and D.W.Turner, J.Chem.Soc., Faraday Trans., II, 69, 196 (1973).
21. C.Batich, P.Bischof, and E.Heilbronner, J.Electron.Spectr., 1, 333 (1973).
22. V.V.Zverev and Yu.P.Kitaev, "Mekhanizmy Geteroliticheskikh Reaktsii" (The Mechanisms of Heterolytic Reactions), Izd.Nauka, Moscow, 1976, p.271.
23. L.L.Miller, V.R.Keck, T.Kolnig, and N.Tuttebe, J.Amer.Chem.Soc., 95, 5075 (1973).
24. E.Haselback and H.D.Martin, Helv.Chim.Acta, 57, 472 (1974).
25. K.N.Houk, J.K.George, and K.E.Duke,Jnr., Tetrahedron, 30, 523 (1974).
26. T.Koopmans, Physica, 1, 104 (1933).
27. M.J.S.Dewar, "The Molecular Orbital Theory of Organic Chemistry" (Translated into Russian), Izd. Mir, Moscow, 1973.
28. W.C.Richards, J.Mass Spectrom.Ion.Phys., 2, 419 (1969).
29. H.D.Pamuk, Theor.Chim.Acta, 28, 85 (1972).
30. F.Brogli, P.A.Clearc, and E.Heilbronner, Angew. Chem.Intern.Edit., 12, 422 (1973).
31. E.Heilbronner, V.Hornung, F.H.Pinkerton, and S.F.Thomas, Helv.Chim.Acta, 55, 289 (1972).
32. J.Spanget-Larsen, J.Electron.Spectr., 3, 369 (1974).
33. V.I.Vovna, F.I.Vilesov, and S.N.Lopatin, Optika i Spektrosk., 36, 436 (1974).
34. J.P.Maier and D.W.Turner, J.Chem.Soc.Faraday Trans., II, 68, 711 (1972).
35. A.Schweig and W.Thiel, J.Electron.Spectr., 3, 27 (1974).
36. C.R.Brundle, M.B.Robin, N.A.Kuebler, and H.Basch, J.Amer.Chem.Soc., 94, 1451, 1466 (1972).
37. J.C.Bunzli, D.C.Frost, and C.A.McDowell, J. Electron.Spectr., 1, 481 (1972/1973).
38. P.Dechant, A.Schweig, and W.Thiel, Angew.Chem., Intern.Edit., 12, 308 (1973).
39. K.Kimura, S.Katsumata, V.Achiba, H.Matsumoto, and S.Naganura, Bull.Chem.Soc., Japan, 46, 373 (1973).
40. H.Ochling, W.Schäfer, and A.Schweig, Angew. Chem., 83, 723 (1971).
41. H.Ochling and A.Schweig, Tetrahedron Letters, 4941 (1970).
42. W.Schäfer, A.Schweig, F.Bickelhanpt, and H.Wermer, Angew.Chem., 84, 993 (1972).
43. A.Schweig, W.Schäfer, and K.Dimroth, Angew. Chem., 84, 636 (1972).
44. W.Schäfer, A.Schweig, G.Märkl, and K.-H.Heier, Tetrahedron Letters, 3743 (1973).
45. W.Schäfer, A.Schweig, F.Bickelhaupt, and R.Vermeer, Rec.Trav.chim., 93, 17 (1974).
46. C.Batich, E.Heilbronner, V.Hornung, A.J.Ashe, D.T.Clark, V.T.Cobley, D.Kilcast, and J.Scanlan, J.Amer.Chem.Soc., 95, 928 (1973).
47. H.L.Hase, A.Schweig, H.Hahn, and J.Badloff, Tetrahedron, 29, 475 (1973).
48. A.W.Potts, H.J.Lempka, D.G.Streets, and W.C.Price, Phil.Trans., A268, 59 (1970).
49. A.W.Potts and W.C.Price, Proc.Roy.Soc., A326, 181 (1972).
50. S.Cradock, E.A.V.Ebaworth, W.J.Savage, and R.A.Whiteferd, J.Chem.Soc.Faraday Trans., II, 68, 934 (1972).
51. S.Cradock and D.W.H.Rankin, J.Chem.Soc., Faraday Trans., 68, 940 (1972).
52. P.J.Bassett and D.R.Lloyd, J.Chem.Soc., Dalton. Trans., 248 (1972).
53. D.Betteridge, M.Thompson, A.D.Baker, and N.R.Kemp, Analyt.Chem., 44, 2005 (1972).
54. J.L.Berkosky, F.O.Ellison, T.H.Lee, and J.Rabalis, J.Chem.Phys., 59, 5342 (1973).
55. A.H.Cowley, M.J.S.Dewar, D.W.Goodman, and J.R.Schweiger, J.Amer.Chem.Soc., 95, 6506 (1973).
56. A.H.Cowley, M.J.S.Dewar, D.W.Goodman, M.S.Padolina, and J.R.Schweiger, "Abstracts of the Vth International Conference on Organophosphorus Chemistry, Gdansk, 1974".
57. A.H.Cowley, M.J.W.Dewar, D.W.Goodman, and M.S.Padolina, J.Amer.Chem.Soc., 96, 2648 (1974).
58. V.V.Zverev, F.I.Vilesov, V.I.Vovna, S.N.Lopatin, and Yu.P.Kitaev, Izv.Akad.Nauk SSSR, Ser.Khim., 1061 (1975).
59. W.Schäfer and A.Schweig, Angew.Chem., 84, 898 (1972).

60. W.Schäfer, A.Schweig, G.Märkl, H.Hauptmann, and F.Mathey, Angew.Chem., 85, 140 (1973).
61. T.B.Debies and J.W.Rabalais, Inorg.Chem., 13, 308 (1974).
62. R.H.Staley and J.L.Beauchamp, J.Amer.Chem. Soc., 96, 6252 (1974).
63. S.Elbel, H.Bergmann, and W.Enβlin, J.Chem.Soc., Faraday Trans., II, 70, 555 (1974).
64. H.Schmidt, A.Schweig, F.Mathey, and G.Muller, Tetrahedron, 31, 1287 (1975).
65. M.F.Lappert, J.B.Pedley, B.T.Wilkins, D.Stelzer, and E.Unger, J.Chem.Soc., Dalton.Trans., 1207 (1975).
66. A.H.Cowley, M.J.S.Dewar, J.W.Gilje, D.W.Goodman, and J.K.Schweiger, Chem.Comm., 340 (1974).
67. A.H.Cowley, M.J.S.Dewar, and D.W.Goodman, J.Amer.Chem.Soc., 97, 3653 (1975).
68. H.Bock, Pure and Appl.Chem., 44, 343 (1975).
69. H.Goetz, F.Marschner, H.Juds, and H.Pohle, Phosphorus, 6, 137 (1976).
70. J.H.Hiller and V.R.Saunders, Chem.Comm., 316, 1510 (1970).
71. J.H.Hiller and W.R.Saunders, Trans.Faraday Soc., 66, 2401 (1970).
72. H.L.Hase, A.Schweig, H.Hahn, and J.Radloff, Tetrahedron, 29, 469 (1973).
73. L.V.Gurvich, "Energii Razryva Khimicheskikh Svyazei. Potentsialy Ionizatsii i Srodstvo k Protonu" (Chemical Bond Dissociation Energies, Ionisation Potentials, and Proton Affinities), Izd.Nauka, Moscow, 1974.
74. H.Boch, C.Wagner, and J.Kroner, Tetrahedron Letters, 3713 (1971).
75. T.P.Debies and J.W.Rabalais, J.Electron.Spectr., 1, 355 (1973).
76. J.P.Meier and D.W.Turner, Discuss.Faraday Soc., 54, 149 (1972).
77. O.A.Raevskii, A.N.Vereshchagin, Yu.A.Donskaya, F.G.Khalitov, I.G.Malakhova, and E.N.Tsvetkov, Izv.Akad.Nauk SSSR, Ser.Khim., 453 (1974).
78. O.S.Khalil, J.L.Meeks, and S.P.McGlynn, J. Amer.Chem.Soc., 95, 5876 (1973).
79. J.W.Rabalais and R.J.Colten, J.Electron.Spectr., 1, 83 (1972).
80. V.V.Zverev, V.I.Vovna, T.N.Pylaeva, Yu.P.Kitaev, and F.I.Vilesov, Zhur.Org.Khim., 11, 1719 (1975).
81. G.Wagner and H.Bock, Ber., 107, 68 (1974).
82. B.A.Sweigait and D.W.Turner, J.Amer.Chem. Soc., 94, 5592, 5599 (1972).
83. A.D.Walsh, J.Chem.Soc., 2301 (1953).
84. D.Santry, J.Amer.Chem.Soc., 90, 3309 (1968).
85. N.M.Zaripov, V.A.Naumov, and L.N.Tuzova, Dokl.Akad.Nauk SSSR, 218, 1132 (1974).
86. L.V.Vilkov, L.S.Khaikin, and V.V.Evdokimov, Zhur.Strukt.Khim., 13, 7 (1972).
87. H.Bock and W.Fuβ, Ber., 104, 1687 (1971).
88. V.I.Vovna, Candidate's Thesis, Leningrad State University, Leningrad, 1974.
89. V.I.Vovna, S.N.Lopatin, R.Paetzold, F.I.Vilesov, and M.E.Akopyan, Optika i Spektrosk., 34, 868 (1973).
90. V.I.Vovna, S.N.Lopatin, R.Paetzold, F.I.Vilesov, and M.E.Akopyan, Optika i Spektrosk., 36, 173 (1974).
91. V.I.Vovna, S.N.Lopatin, R.Paetzold, and F.I.Vilesov, Khim.Vys.Energii, 9, 9 (1975).
92. F.I.Vilesov, S.N.Lopatin, V.I.Vovna, R.Paetzold, and K.Niendorf, Z.phys.Chemie, (Leipzig), 255, 661 (1974).
93. F.I.Vilesov and S.N.Lopatin, Zhur.Tekh.Fiz., 42, 176 (1972).
94. K.Heinz, H.Bock, and H.Dieck, Angew.Chem., 87, 197 (1975).
95. D.P.Santry and G.A.Segal, J.Chem.Phys., 47, 158 (1967).
96. H.Maramann, L.C.D.Groenweghe, L.J.Szhaad, and J.R.Van Wezer, J.Amer.Chem.Soc., 92, 6107 (1970).
97. R.Paetzold and K.Niendorf, Z.phys.Chem. (Leipzig), 256, 361 (1975).
98. D.Ya.Osokin, J.A.Safen, and J.A.Nuretdinov, Org.Magn.Res., 4, 831 (1972).
99. T.K.Semin, T.A.Babushkina, and G.G.Yakobson, "Primenenie Yadernogo Kvadrupol'nogo Rezonansa v Khimii" (Chemical Applications of Nuclear Quadrupole Resonance), Izd.Khimiya, Leningrad, 1972.
100. M.I.Shanduk, N.I.Yanchuk, and A.P.Grekov, Zhur.Org.Khim., 10, 2357 (1974).
101. L.V.Vilkov, N.I.Sadova, and I.Yu.Zil'berg, Zhur. Strukt.Khim., 8, 528 (1967).
102. H.Oberhammer, Z.Naturforsh., 28A, 1170 (1973).
103. C.J.Bullen, D.S.Stephena, and R.J.Wade, J.Chem. Soc.(A), 1804 (1969).
104. K.A.Ostoja Starzewski, H.Tom Dieck, and H.Bock, J.Organometal.Chem., 65, 311 (1974).

Arbuzov Institute of Organic and
Physical Chemistry, Kazan Branch
of the USSR Academy of Sciences