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Intramolecular Electronic Interactions in Phosphorus Compounds in the Light of Recent Structural Studies

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The nature and mechanism of intramolecular electronic interactions in compounds of three- and four-coordinate phosphorus have been critically examined on the basis of a review of the results of the study of their three-dimensional structure and physical properties. The high π-acceptor power of phosphorus-containing groups, capable of stabilising conformations with the *trans*-orientation of the interacting orbitals of the donors (the *n*-orbitals of the unshared electron pairs of the heteroatoms or the π-orbitals of unsaturated systems) and the acceptors (bonds of the phosphorus atom) has been proved.
The bibliography contains 193 references.

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I. INTRODUCTION

The development of the theory of intramolecular electronic interactions is related to the experimental and theoretical analysis of more complex hetero-organic compounds, among which a leading place is occupied by organophosphorus compounds (OPC). The exceptional ability of the phosphorus atom to take part in electronic interactions of the most varied types, due primarily to the possibility of a change in the coordination number of this atom from one to six, is well known. The presence of unoccupied orbitals and unshared electron pairs (UEP), the high polarisability and polarity of the bonds formed by phosphorus, and the ability to form donor–acceptor and multiple bonds make it possible to construct any required model of OPC for the study of intramolecular electronic interactions.

An important contribution to the solution of the problem of the nature of electronic effects has been made by the concepts of three-dimensional structure. The combined study of the three-dimensional and electronic structure makes it possible to formulate fundamentally new, deeper, and comprehensive ideas on the nature, mechanism, location, and spatial-directed character of intramolecular electronic interactions. For organic compounds, these ideas have made it possible to approach an understanding of general regular features, and an elegant and systematic structural theory has been developed[1,2], in which the qualitative model of a one-electron molecular orbital has been used as the theoretical basis for discussing most problems. This approach makes it possible to develop a general theory of three-dimensional structure and chemical reactivity.

The development of the quantum-mechanical theory of conformational analysis has led to the introduction of the following types of intramolecular electronic interactions, not dealt with in the classical theory of electronic displacements: 1) the π- and σ-interactions of non-bonded atoms; 2) π- and σ-conjugation interactions; 3) geminal interactions; and 4) the effects of the ionic character of bonds. In the opinion of Epiotis and co-workers[1], these interactions form an "alphabet" for predicting the characteristic structural features of organic compounds, and to a considerable extent make it possible to model systems with a required geometry. A monograph by Epiotis[2] clearly defines the three-dimensional and geometric restrictions and various physical characteristics (displacement of electron density, ionisation potentials, etc.) indicating the existence of different types of electronic interaction. This makes possible the further development of the theory as applied to more complex hetero-organic compounds on the basis of available factual material.

The electronic structure of OPC and the effects of the mutual influence of atoms which they show have been the subject of many studies. Most of them were carried out in the nineteen-sixties from the viewpoint of the "*d* orbital concept",[4,5] which has often been criticised[6], so that up to the present, the problem of the participation of the *d* orbitals of the atoms of non-transition elements in chemical bond formation has not been resolved. The approach in the form of a correlation analysis has been fairly widely developed[7–9]. Overall, however, an urgent need has grown for a systematic analysis of intramolecular electronic interactions in OPC on the basis of present-day views on the nature and mechanism of electronic interactions. The foundation for this approach should be provided by the extensive factual data on the conformational behaviour of OPC and their physical properties. The results of the conformational analysis of OPC have been summarised in a number of reviews[10–12]. Extensive additional information on the geometric parameters, the nature of electron displacements, and the energy characteristics of boundary orbitals is provided by various physical methods. Many of these results (electron and X-ray diffraction, NMR spectroscopy) are given in reviews of the conformational analysis of OPC,[10–12] and others are given in reviews of the use of photoelectron spectroscopy[13–15], dipole moments, and the Kerr effect[16,17] in the chemistry of OPC; an appreciable proportion of the results have been published in the past five years only in original papers.

The present review examines from this viewpoint the compounds of three- and four-coordinate phosphorus [P(III) and P(IV)] in order to detect and identify intramolecular electronic interactions. The important role played by the electronic nature and structure of reagents in determining a preferred reaction path (including OPC [18]) is well known, so that the development of present-day views on the mecha-

nism of the mutual influence in OPC should stimulate the interest of chemists in revealing the fundamental relationship between three-dimensional structure, electronic structure, and the chemical reactivity of hetero-organic compounds.

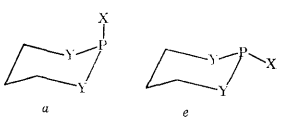
II. ELECTRONIC INTERACTIONS OF TERVALENT PHOSPHORUS WITH *n*-ELECTRON-DONOR SUBSTITUENTS

The directed study of various properties of cyclic P(III) compounds in the last ten years has provided a basis for a deep analysis of the effects of the mutual influence of atoms in the systems studied. The most comprehensive and complete studies by various physical methods have been carried out for 2-X-1,3,2-diheterophosphorinanes. The following brief review of studies carried out in this field will be restricted to an examination of the most fundamental characteristics of the molecule in order to investigate the nature and mechanism of intramolecular electronic interactions.

1. THE MANIFESTATION OF INTERACTION IN EXPERIMENTAL CHARACTERISTICS

a) Three-dimensional Structure

The most complete and extensive conformational studies have been carried out for 2-X-1,3,2-diheterophosphorinanes. The results have been summarised in a number of reviews[10-12, 19,20]. The conformations of cyclic systems with a P atom in the ring are determined by the nature of its intracyclic substituents. If this is a heteroatom (Y = NR, O, S), the chair form with the exocyclic bond in the axial (*a*) position predominates.



a *e*

An exception was found for the dialkylamino-group (X = NR_2, Y = O).[21-27] The observed deviations are due chiefly to steric interactions. The replacement of the heteroatoms by carbon atoms leads to a decrease in the energetic preference for the *a*-form, the proportion of which increases when heteroatoms with a small volume are introduced in positions 3 and 5 relative to the phosphorus atom. This clearly defined trend towards the stabilisation of one form, which is unfavourable in the light of steric repulsion effects (for cyclohexane derivatives, the *e*-conformation is preferred) indicates the strictly stereospecific nature of the effect, leading to an energy gain in favour of the *a*-orientation of the exocyclic substituent.

b) Electron Density Distribution

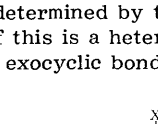
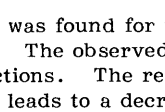
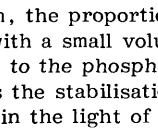
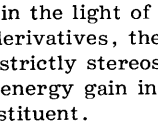
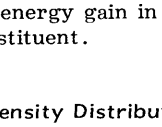
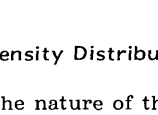
Change in the nature of the exocyclic substituent X in 2-X-1,3,2-dioxaphosphorinanes (Y = O) leads to consideragle changes in the electron density distribution in the phosphorus-containing part of the molecule. Quantitative information on the change in the polarity of the bonds formed by phosphorus in the compounds being considered has been obtained using isoelectric maps (Table 1).[16] These data indicate that the phosphorus bonds have a high electron mobility. The distinct differences in the properties of the substituents can be seen from Table 1: the chlorine atom[28] and the phenoxy-group[29,30] have acceptor properties, leading to the transfer of electron density from the ring oxygen and phosphorus atoms towards the substituent X; the dialkylamino-group is a UEP donor, and the migration of electron density takes place in the opposite direction, towards the ring oxygen atoms[27]. In 2-ethoxy- [16,29] and 2-phenyl-1,3,2-dioxaphosphorinanes[31], the nature of the electron density distribution differs little from that in the symmetrically substituted compounds[16], although the first compound shows slight non-equivalence of the P–O bonds. The increase in the polarity of the P–Cl bond in the ring compared with PCl_3 corresponds to a decrease in the frequency of the ^{35}Cl NQR signal (20.19 MHz compared with 26.208 MHz for PCl_3).[32]

Table 1. Dipole moments of the phosphorus bonds in 2-X-1,3,2-dioxaphosphorinanes and compounds PX_3.

Group	*m*, D	Substituent X				
		O (Ph) [30]	Cl [28]	O [R] [16, 29]	Ph [31]	N (R)$_2$ [27]
O_2PX	m_{P-O}	−0.8	−0.72	−0.32	−0.06	0.65
O_2PX	m_{P-X}	0.22	0.92	0.14	−0.95	0.37
PX_3	m_{P-X}	0	0.56	0	−1.18	−0.25

Note. Numbers in square brackets denote references (Ed. of Translation).

Table 2. Experimental parameters of cyclic systems with a P–Cl bond.

No.	Compound	ν, MHz [32]	l_{P-Cl}, Å [34]	γ_{P-Cl}, Å^3 [16]
(I)		15.797	2.190	—
(II)		17.08	—	—
(III)		17.6	2.174	—
(IV)		18.64	—	—
(V)		19.86	2.105	0.34
(VI)		20.19	2.128	−0.67
(VII)		21.55 22.19	—	—
(VIII)		24.524	2.153 [35]	—
(IX)		25.79	—	−1.33
(X)	PCl_3	26.208	2.043	2.66

Notes: ν is the frequency of the signal in the ^{35}Cl NQR spectrum, l_{P-Cl} is the P–Cl bond length, and γ_{P-Cl} is the anisotropy of the polarisability of the P–Cl bond.

Note. Numbers in square brackets denote references (Ed. of Translation).

The frequency of the ^{35}Cl NQR signal, which reflects the shielding of the chlorine atom, is used to estimate the polarity of different bonds formed by the chlorine atom[33].

The ^{35}Cl NQR spectra of 2-X-1,3,2-diheterophosphorinanes have been studied[34]. The experimental data obtained (Table 2) make it possible to follow the change in the dipole moment of the P–Cl bond (m_{P-Cl}) with change in the nature of the substituent Y in the fragment Y_2PCl; the frequency decreases considerably (from 26.208 MHz to 17.08 MHz), so that the dipole moment increases in the following order of substituents: Cl > S > O > NR. On going from five- to six-membered rings, the frequency increases by approximately 1 MHz. The greatest displacement of electron density to the chlorine atom is observed for the 1,3,2-diaza-derivatives.

c) Bond Polarisability

The anisotropy of the bond polarisability (γ) is one of the most sensitive characteristics of different types of intramolecular electronic interaction. 2-X-1,3,2-dioxaphosphorinanes show extensive changes in the anisotropy of the polarisability of the P–O and P–X bonds, compared with the corresponding symmetrically substituted compounds[16] (Table 3). With increase in the acceptor properties of the substituent X in 2-phenoxy-[30] and 2-chloro-1,3,2-dioxaphosphorinanes[28] there is an increase in the longitudinal component of the polarisability ellipsoid of the P–O bonds. In the chloro-anhydride (VI) there is a marked increase in the perpendicular component of the polarisability ellipsoid of the P–Cl bond b_T and a corresponding decrease in γ ($\gamma = -0.67$ Å^3), compared with PCl_3 ($\gamma = 2.66$ Å^3).[28] An even greater increase in b_T is observed for 2-chloro-1,3,2-dithiaphosphorinane (IX) (see Table 2).[38] In the chlorophosphite series, the changes in γ for the P–O and P–Cl bonds of the O_2PCl group are inversely proportional: decrease in the longitudinal component for the P–Cl bond is accompanied by an increase in the longitudinal component for the P–O bond[16].

Table 3. Anisotropy of the polarisability of the phosphorus bonds in 2-X-1,3,2-dioxaphosphorinanes and in compounds PX_3.

Group	γ, Å^3	Substituent X			
		Cl [28]	O (Ph) [30]	C_{sp^2} (Ph) [36]	N (Me_2) [37]
O_2PX	γ_{P-O}	3.27	3.11	1.95	2.12
O_2PX	γ_{P-X}	−0.67	2.35	4.0	2.24
PX_3	γ_{P-X}	2.66	−0.59	--	2.81

Note. Numbers in square brackets denote references (Ed. of Translation).

d) Bond Lengths

The data obtained up to the present on the P–Cl bond lengths in various 2-X-1,3,2-diheterophosphorinanes and their five-membered analogues (Table 2) show wide changes in the P–Cl values in a range of 0.15 Å [from 2.043 Å in compound (X) to 2.190 Å in compound (I)]. The P–Cl bond length increases on going from PCl_3 to the dioxa-derivatives and then to the dithia- and on to the diaza-derivatives, which show the greatest increase in the antibonding character of this bond. A functional relationship has been established between the values of the anisotropy of the polarisability γ and the bond length l.[16,38] The bonding increases with increase in the positive contribution to γ. The greatest increase in the transverse component of the P–Cl bond, that is the greatest increase in the antibonding character of the bond, is to be expected in the oxaza- and diaza-derivatives of the chloro-anhydrides of acids of tervalent phosphorus.

e) Valence Angles

An interesting characteristic of the geometric structure of 2-X-1,3,2-diheterophosphorinanes with a P–X bond in the α-position, and of many acyclic P(III) compounds, is the increase in the valence angles at a heteroatom (O, N) adjoining the P atom, and there is a clearly defined trend towards the sp^2 hybrid state of the heteroatom. The intracyclic angle at the oxygen atom is close to 120° in 2-chloro-1,3,2-dioxaphosphorinane[39] and 5-spiro-2-methoxy-1,3,2-dioxaphosphorinane[40]. The sum of the angles at the nitrogen atom in 1,3,2-oxaza-[41,42] and diazaphospholans[43] and in amidophosphites[44–47] is close to 360°. According to Dewar's calculations[48], the planar form for the nitrogen atom becomes energetically favourable only when the conjugation energy $\delta E_\pi \geq 18$ kcal mole^{-1}. This condition is not satisfied even for aniline and amides. The flattening of the pyramid of a nitrogen atom situated next to phosphorus has been discussed many times[49], but no satisfactory explanation has yet been found; it is clear only that a non-standard sp^2 electronic state of the heteroatoms indicates considerable interactions with the "liberated" p unshared electron pair of the heteroatom.

f) Energies of the Highest Occupied Molecular Orbital (HOMO)

The interpretation of photoelectron spectra in the approximation of Koopmans' theorem makes it possible to estimate the orbital energies, which are equated to the ionisation potentials. Studies of this kind have been carried out for 2-X-1,3,2-dioxaphosphorinanes with X = NMe_2, OMe, Cl;[50,51] the ionisation energies of the HOMO n_P, n_N, and n_O have been obtained. There is no splitting of the orbitals of the unshared electron pairs (UEP) of the nitrogen and phosphorus atoms in the 2-dimethylamino-derivative. The ionisation potential of the orbital n_P does not obey the additivity rule, because of the interaction of the UEP of the phosphorus atom with the UEP of the adjacent heteroatoms: $n_O - n_P$, $n_N - n_P$, $n_{Cl} - n_P$. The ionisation potentials of the UEP of the oxygen atoms undergo smaller changes; the n_O orbital in the dimethylamino-derivative is destabilised to a much greater extent (10.0 eV), compared with chlorophosphite (10.76 eV). Overall, the cyclic compounds show an increase in the same sense in the energies of all the highest occupied molecular orbitals, and this can be attributed to the difference in the direction of the $n-\sigma^*$ hyperconjugation interaction.

2. THEORETICAL INTERPRETATION OF EXPERIMENTAL DATA

All the above factors prove the high electron lability of the Y_2PX group. The observed electronic effect (or set of effects) is strictly stereospecific, and leads to stabilisation of the α-orientation of the polar bond P–X in the 2-X-1,3,2-diheterophosphorinanes. In all cases the phosphorus atom is adjacent to a heteroatom whose electronic state, according to data on the valence angles, is close to sp^2 hybridisation, so that the heteroatom acts as a p_π-UEP donor. The phosphorus atom, together with the adjoining bonds, shows

clearly defined π-electron-acceptor properties. The π-electron-acceptor effect is apparently not particular but universal in character, and is the main reason for the marked difference between the properties of the compounds of the elements in period II and subsequent periods. This problem was recently examined for compounds of silicon[52,53], arsenic[54,55], sulphur, and phosphorus[55,56]. The problem is of considerable importance for an understanding of the characteristic features of the chemical behaviour of heteroorganic compounds of the non-transition elements as a whole.

There arises the question of whether the high electron lability of P(III) compounds can be interpreted on the basis of existing ideas on intramolecular electronic interactions.

a) $d_{\pi}-p_{\pi}$ Interaction

The traditional explanation of the π-electron-acceptor properties of the phosphorus atom is related to the presence of its unoccupied 3*d* orbitals[4,5]. It is considered that $d_{\pi}-p_{\pi}$ conjugation leads to an increase in the strength of the bonding between the phosphorus atom acting as acceptor and the neighbouring heteroatom acting as donor. For 2-X-1,3,2-diheterophosphorinanes, the participation of the *d* orbitals of the phosphorus atom should have led to only an increase in the double-bond character of the bonds. In fact, however, as noted above, an increase in the antibonding character of the exocyclic P–Cl bond is observed. Even in those cases where the intracyclic substituents Y have a higher electronegativity (Y = NR, O) than the chlorine atoms in PCl_3 (which undoubtedly should have led to the participation of the d_{π} orbitals in bonding as a result of the increase in the positive charge on the central atom), the P–Cl bond is destabilised, compared with the same bond in PCl_3. Analysis of the direction of the displacement of electron density also indicates that the participation of 3*d* orbitals is unlikely. For $d_{\pi}-p_{\pi}$ conjugation, the displacement of electron density should take place towards the P atom; it follows from the data in Table 1, however, that for each case it is possible to show examples of the opposite direction of the effect (in 2-dialkylamino-1,3,2-dioxaphosphorinanes, the electron density is displaced towards the ring oxygen atoms). Moreover, the material obtained indicates that the effect is not localised on the central atom, and the electron acceptor in all cases is the neighbouring bond (the P–Cl bond in 2-chloro-1,3,2-diheterophosphorinanes).

Thus the increase in the antibonding character of the acceptor bond, the direction of the displacement of the electronic charge, and the extension of the transfer of electron density beyond the phosphorus atom towards the acceptor bond cast doubt on the possibility of interpreting the effect on the basis of the concept of $d_{\pi}-p_{\pi}$ conjugation.

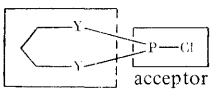
b) Electrostatic Geminal Interaction

Significant (analogous in strength and direction) effects of electron density displacement have been observed for organic compounds of the elements of Group IVb (E = Si, Ge, Sn) containing the group X–C(–)–E (X = Hal, O, N, S).[53] The magnitude of the interaction, as in the case of 2-X-1,3,2-diheterophosphorinanes, does not correspond to the electronegativity of the atoms and the inductive effect of the substituents. This effect has been called the geminal interaction of atoms or the α-effect+.[53] Systematic studies of the ^{35}Cl NQR spectra of compounds containing the Cl–C(–)–Si group led Feshin and co-workers[53] to conclude that the anomalous properties of the compounds are due to the electrostatic interaction of the charge of the atom E with the electron cloud of the C–X bond. The hypothesis of a possible electrostatic interaction by a field effect mechanism was verified for compound (VI).[59] Calculation showed that the dipole moment of the P–Cl bond should increase by 0.23 D. Under the influence of the electric field of the P–Cl dipole [0.56 D in compound (X) or 0.92 D in compound (VI), see Table 1], electron density is displaced from oxygen to phosphorus, and the dipole moment changes by 0.12 D or 0.17 D respectively. According to the isoelectric maps, however, the moment of the P–O bond increases by 0.72 D on going from the symmetrically substituted phosphites to compound (VI).[28] Thus electrostatic interactions, although acting in the appropriate direction, cannot fully explain the extensive changes in electron density taking place.

c) $n-\sigma^*$ Hyperconjugation Interaction

The stabilisation of the *a*-orientation of a polar substituent in 1,3,2-diheterophosphorinanes lies within the framework of the anomeric effect, the nature of which has been discussed many times[60] and is now related to the interaction between the *p*-type UEP of the ring heteroatom and the antibonding MO of the exocyclic polar bond. Moreover, the increase in the polarity of the P–Cl bond, the increase in its length, and the decrease in the frequency of the ^{35}Cl NQR signal, observed for 2-chloro-1,3,2-dioxaphosphorinane, correspond to the variations in these parameters in α-chloroethers containing the Cl–C–O group.[1,61–65] The anomalous behaviour of α-chloroethers has been widely studied, and has been called the α-effect,[61] the mechanism of which (the interaction of the *p* orbital of the UEP of the oxygen atom with the antibonding orbital of the C–Cl bond $n_O-\sigma^*_{C-Cl}$[61–65] is analogous to that of the anomeric effect. The possible existence of this interaction is 2-X-1,3,2-diheterophosphorinanes has also been examined in detail[59].

In 2-chloro-derivatives (XI), two fragments are clearly distinguished: an electron-acceptor fragment with a P–Cl bond, and an electron-donor fragment with 1,3-heteroatoms Y;[39–43,47] the best electron donor is a semi-localised orbital of the *n**-type formed by the reaction of two equivalent *p* orbitals of the UEP of the heteroatoms Y.[66,67]



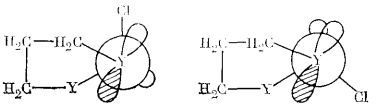
(XI)

According to the values of the ionisation potentials of the orbitals of the UEP of the atoms in OPC,[15] the donor power decreases in the following order: $n_N > n_S > n_P > n_O > n_{Cl}$; the increase in the π-electron-donor power of the sulphur atom compared with the oxygen atom is attributed to the fact that it adjoins the low-lying unoccupied molecular orbital (LUMO) (σ^*_{P-Cl}).[68]

+The term "α-effect" has another meaning[57,58], which is used later in the present review (Russian page 603). To avoid ambiguity in terminology, and following Feshin and co-workers[53], the effect being discussed here will be called the effect of the geminal interaction of the atoms.

The acceptor power of bonds is also closely related to their ionisation potentials[1,15]; it increases on going to bonds formed by elements of period III. Unfortunately, data on the ionisation potentials of the phosphorus bonds are not so unambiguous as the values of the ionisation potentials of the higher-lying orbitals of the UEP.

The donor and acceptor fragments of the molecules of 2-X-1,3,2-diheterophosphorinanes interact with one another in different ways in the two alternative conformations with *a* and *e* P–Cl bonds.



a—P—Cl; (T) *e*—P—Cl; (G)

The *e* position of the P–Cl bond is characterised by the gauche orientation (G) of *n* and the P–Cl bond, and the axial position by the *trans*-orientation (T). The $n-\sigma^*$ interaction is a maximum for the T-orientation of the orbitals being considered[1]. This interaction leads to considerable stabilisation of the T conformer, and indicates that there is transfer of the charge of the *p*-UEP of the Y atoms to the P–Cl bond; this also leads to an increase in the charge on the chlorine atom and a decrease in the charge on the ring Y atoms. The greatest effect of electron density transfer is observed for 2-chloro-1,3,2-diazaphosphorinanes (the frequency of the ^{35}Cl NQR signal is a minimum), since the nitrogen atoms are better electron donors than the oxygen and sulphur atoms. The sulphur atoms in turn are characterised by stronger donor properties than the oxygen atom. This explains why the length of the P–Cl bond and the anisotropy of its polarisability have intermediate values, compared with the dioxa- and diaza-derivatives. According to the ^{35}Cl NQR frequencies, however, the transfer of electron density is slight; this is related to the diffuse character of the UEP of the sulphur atom compared with the 2*p* orbitals of the UEP of oxygen and nitrogen. The latter are not diffuse, the charge of the two electrons is concentrated in a small region, and for them the $n-\sigma^*$ conjugation is reflected in the form of the charge transfer.

The interaction should also lead to an increase in the length of the acceptor bond[1]; the bond formed by the donor atom, however, may become stronger (a decrease in the length of the C–O bond in α-chloroethers is observed[65,69]). In 2-chloro-1,3,2-diheterophosphorinanes, the P–Cl bond in fact becomes longer, the increase being greater, the greater the donor power of the heteroatoms Y (in the order O < S < N).

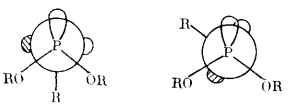
Change in the nature of the substituent X (in the P–X bond) should be reflected in the magnitude of the $n-\sigma^*$ interaction. The ionisation potentials of the bonds P–O(R) and P–C are approximately the same, and their absolute values are greater than those for the P–Cl bond[15,67], so that for the corresponding compounds the interactions are less clearly defined.

d) The α-Effect and the Acceptor Power of Bonds

Comparison of the above data for OPC and published data data[1,61–65] for α-chloroethers indicates that the effect of $n-\sigma^*$ hyperconjugation interaction in OPC is much greater. Calculations show that a position next to a low-lying unoccupied molecular orbital leads to an increase in the π-electron-donor power of heteroatoms[68]. In the present section, the factors leading to an increase in the acceptor power of bonds are examined. This increase is due to the decrease in the energy of the σ^* orbital, which is to a large extent related to the destabilisation of the acceptor bond. In the case of the P–Cl bond, the increase in the antibonding character is due to the familiar α-effect, typical of systems containing adjacent UEP.[3,57,58] The effect itself is often related to the stabilisation of the transition state[57], so that until recently, its influence on the physical properties was not examined. According to quantum-mechanical calculations[58], however, the α-effect is characterised formally by the destabilisation of the ground state, due to the interaction of the UEP of adjacent heteroatoms. Often (but not always), conditions are created for an antisymmetric combination of UEP, which leads to a more diffuse distribution of the electron density of the occupied molecular orbital with a nodal plane and perpendicular to the line of the bond; in the opinion of Bentrude and Tan[23], this should lead to a high "non-uniformity" of the polarisability of the bonds.

In this respect, the P–Cl bond is apparently one of the best acceptors; it has a high polarisability $b = 10.04$ Å^3,[16] due to the diffuse distribution of the electron density. Moreover, the destabilising repulsion of the n_P-n_{Cl} orbitals is appreciable for all orientations of the n_P orbital. In most other cases, however, the molecule can avoid unfavourable interactions of adjacent UEP by conformational rearrangements.

For other bonds formed by phosphorus, in which it is next to elements of groups V and VI b, the presence or absence of the α-effect depends on the conformational characteristics. In 2-alkoxy-1,3,2-dioxaphosphorinanes, the P–O bonds differ in their rotational-isomer properties: for steric reasons, the exocyclic bond cannot achieve the T-conformation characteristic of the ring bonds, and it has the G-orientation[29]



$n_O \perp n_P$; (T) $n_O \parallel n_P$; (G)

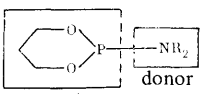
In the G-conformation, the repulsion between the UEP of the oxygen and phosphorus atoms n_O-n_P is a maximum. This conclusion is confirmed by an analysis of the photoelectron spectra. Studies of a whole series of trialkyl phosphites, in which there is a gradual change from GGG structures to structures with the T-orientation of all three alkoxy-groups[50,51], show that the n_O-n_P interaction is a maximum in the G-conformation, and can be estimated (by means of the parameter β_{OP}^{π}) as 0.58 eV. The interaction between the UEP of the oxygen and phosphorus atoms is so great that it leads to extensive variation in the ionisation potential of the orbital n_P (of the order of 1 eV), depending on the rotational-isomer properties of the P–O bonds.

Thus P–O bonds which are non-equivalent according to their conformational characteristics also differ in their energy parameters; the antibonding character of the exocyclic bond increases considerably, and it acts as the acceptor of the UEP of the ring oxygen atoms. The effect is reflected in the relative increase in the length of the exocyclic P–O bond, compared with the ring bonds (1.626 and 1.616, 1.611 Å according to X-ray diffraction data for 3,9-dimethoxy-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane[40]), and also in the displacement of electron density, detected from the isoelectric maps, from the ring oxygen atoms towards the exocyclic P–O bond[16].

In 2-alkylamino-1,3,2-dioxaphosphorinanes, the α-effect of n_N-n_P repulsion is not detected by photoelectron spectroscopy[50,51]. The absence of splitting of the n_N and n_P orbitals shows that the interaction between them is slight, so that they are oriented at right angles to one another.

e) The Exo-anomeric Effect

The exo-anomeric effect was introduced[70] to explain the stabilisation of the structures with *e* C–O bonds in 2-alkoxytetrahydropyrans. In 2-X-1,3,2-diheterophosphorinanes, the *e* conformation is typical of compounds (XII) (X = NR_2 [10,27])



(XII)

In this compound, the best donor (the dialkylamino-group) is removed beyond the ring[39]. The orbital of the UEP of the nitrogen atom, situated next to P(III), has a comparatively low ionisation potential of 8.65 eV [for compound (XII) with R = Me [51]]. This is 2 eV lower than the ionisation potential of the orbital n_O; thus the $n_N-\sigma^*_{P-O}$ interaction must be comparable in strength and of opposite direction, compared with the $n_O-\sigma^*_{P-Cl}$ interaction in compound (VI). This effect is in fact observed; the displacement of electron density takes place from the exocyclic nitrogen atom in the direction of the P–O bond (see Table 1).[27]

In the compounds being considered, there are optimum structural conditions for $n-\sigma^*$ interaction, in spite of the fact that the dialkylamino-group occupies the equatorial position, and not the axial position typical of all other types of X. For the *e* conformation, the P–O bonds have the GG′ structure, in which the α-effect of the destabilising repulsion of the n_O-n_P orbitals is a maximum, so that the acceptor properties of the bond increase. Since the dialkylamino-group is not fixed, the UEP of the nitrogen atom can always take the T-orientation with respect to the P–O bond, favourable for hyperconjugation interaction. For the *e* position of the dialkylamino-group this should be the so-called perpendicular conformation, in which the UEP of the nitrogen and phosphorus atoms are mutually perpendicular. This structure also follows from an analysis of photoelectron spectroscopic data[51].

The possibility of $n_N-\sigma^*_{P-O}$ interaction for the *a*-position of the P–N bond should be emphasised, but in this case it is difficult for the bulky dialkylamino-group to adopt the perpendicular conformation, favourable for $n-\sigma^*$ interaction. The *a*-conformation becomes the preferred conformation only when the bulky NR_2 group is replaced by less bulky groups: NHR (R = Alk, Ph) [26,71,72] or aziridyl,[26] NPh_2, pyrryl[73], or NCO[74], where the nitrogen atom has a planar structure. In this conformation, however, the acceptor power of the ring P–O bonds, which have the TT structure, is decreased, so that the energy of the $n_N-\sigma^*_{P-O}$ interaction is lower than that in compounds with an *e* P–N bond.

The *e*-conformation has also been established for 2-aminotetrahydrofuran[75]. To explain this, the authors cited introduce all possible types of orbital interaction, without distinguishing the predominant one [including interactions in exactly opposite directions, such as, for example, the interactions $n_O(\sigma\text{-type})-\sigma^*_{C-N}$ and $n_N-\sigma^*_{C-O}$]. The above experimental material for 2-alkylamino-1,3,2-dioxaphosphorinanes, together with an analysis of the characteristic stereochemical features of the bonds, make it possible to distinguish the key orbital interaction of the type $n_N-\sigma^*_{P-O}$.

Thus the combination of P(III) with different heteroatoms leads to a labile electronic system with a clearly defined ability to undergo electron-cloud rearrangement. This lability is due to related effects: the destabilising $n-n$ interaction (the α-effect), leading to an increase in the acceptor properties of the bonds; $n-\sigma^*$ hyperconjugation, strengthened by the α-effect; and the field effect. The magnitude of the displacement of the electron cloud of the UEP, the degree of antibonding character in the bond, and the rearrangement of its polarisability ellipsoid depend on the conformational parameters and on the position of the heteroatoms in the periodic system: the elements of period II are characterised by the transfer of the concentrated electron cloud of the 2*p* orbital of the UEP donor (which is responsible for the manifestation of the effect in changes in the dipole moments of the bonds and the ^{35}Cl NQR frequencies); the bonds of the elements of period III, as acceptor bonds, are more easily polarised, with an increase in their antibonding character, and this leads to an increase in their length and to an increase in the contribution of the perpendicular component of the polarisability tensor.

It should be noted that the observed intramolecular interactions are characteristic not only of cyclic compounds. Many of the above experimental observations for 2-X-1,3,2-diheterophosphorinanes are also observed for acyclic compounds[76,77]. The facts indicate that the effects of hyperconjugation interactions are also revealed to a considerable extent in P(IV) compounds[78].

The change from phosphorus compounds to the corresponding arsenic-containing compounds leads to an increase in the strength of the effect. The study of 2-chloro-,[79] 2-bromo-,[80] and 2-phenyl-1,3,2-dioxa-arsenanes[81] using isoelectric and isoanisotropic maps made possible a quantitative estimation of the degree of displacement of electron density and rearrangement of the bond polarisability ellipsoids. The results show that the observed orbital interactions are characteristic of a wide range of compounds, so that they must be taken into account in the interpretation of data on the physical and chemical properties of compounds.

III. CONJUGATION EFFECTS IN COMPOUNDS OF TERVALENT PHOSPHORUS WITH π-ELECTRON-DONOR SUBSTITUENTS

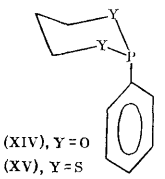
In organophosphorus compounds containing an unsaturated group next to a phosphorus atom, different types of conjugation are possible: $d-\pi$ conjugation, conjugation of the π-electrons of the unsaturated group with the UEP of the P(III) atom, and hyperconjugation of π-electrons with the vicinal bonds of the phosphorus atom. All these forms of intramolecular electronic interaction are strictly stereodirected, so that the study of the spatial characteristics of compounds to a large extent facilitates the identification of the predominant form of conjugation, determining the specific features of the physical and chemical properties of the compounds as a whole.

The monoaryl compounds of tervalent phosphorus $ArPX_2$ (XIII) can be considered, since they are less influenced by steric interactions than the diaryl and triaryl derivatives. The experimental study of these compounds has been carried out mainly in recent years.

1. THREE-DIMENSIONAL STRUCTURE

For monoarylphosphines (XIII) it is possible to have two three-dimensional structures, with parallel (ω = 0°) or perpendicular (ω = 90°) orientation of the UPE of the phosphorus atom (n_P) and the π-orbital of the benzene ring (Fig.1). Many compounds of this type have been studied by electron diffraction and the Kerr effect. An orientation of the *n*- and π-orbitals close to orthogonal has been

established for the following substituents: X = Cl (81°,[82] ~90° [83]); X = F (59° [84]); X = Alk (~90° [85]), X = CN (~90° [86]). The alternative conformation with $\omega \cong 0°$ has been found by infrared spectroscopy for the simplest compound of this series, phenylphosphine[86]. Relaxation NMR measurements have been used to determine the barriers to rotation of the PH_2 and PCl_2 groups (0.17–1.02 kcal mole^{-1} and 0.7 to 4.1 kcal mole^{-1} respectively) about the Ph–P bond[87,88]. Interesting results have been obtained for cyclic compounds with an exocyclic P–Ph bond (XIV) [36] and (XV).[38] In this case there is forced coplanar orientations of the n_P and π orbitals. Marked 1,3-synaxial interactions of the phenyl group in the α-position[31,36,38] rotate the benzene ring at an angle of 90° to the plane of symmetry of the molecule, which contains the UEP of the P(III) atom



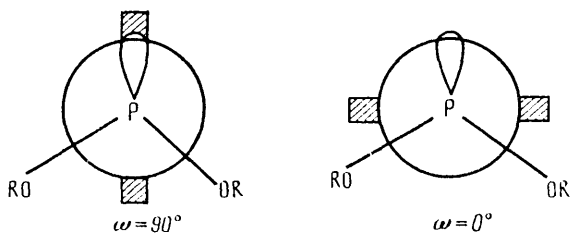


Figure 1. Boundary conformations of the benzene ring in arylphosphines.

The structure of the simplest monophenylphosphines has been studied many times by quantum-mechanical calculations. Non-empirical calculations in an STO-3G basis set for phenylphosphine and phenyldifluorophosphine (X = H, F) show that the UEP of the P(III) atom lies at right angles to the plane of the aromatic ring[89]; when the H, F atoms are replaced by Cl atoms, the alternative conformation (ω = 90°) becomes preferred[89]. Semi-empirical calculations have been carried out by MINDO/3 and MNDO methods with complete optimisation of the geometry of all potentially low-lying conformations[90]. Both methods, and also the CNDO/2 method[91,92], confirm the stabilisation of the structure with an almost parallel orientation of the n and π orbitals in phenylphosphine. The same methods indicate that phenyldimethylphosphine has an analogous structure[90]. For the dichloroderivative (MNDO method[93]), an orthogonal structure has been established, in agreement with the above experimental data.

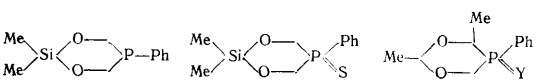
2. SPECTRAL STUDIES OF ELECTRONIC INTERACTIONS IN MONOARYLPHOSPHINES

Indirect information on structure, based on the analysis of the strength of the interaction between the phosphorus-containing substituent group and the π-electrons of the benzene ring, is provided by spectral methods. Most of the work on monoarylphosphines has been devoted to an analysis of the ultraviolet spectra.

The R-band in the range 230–260 nm is considered to be the most characteristic. It is due to the transfer of n_P to the benzene ring ($n \rightarrow \pi^*$ transition). Many authors assume that the intensity of the band is related to the relative orientation of the n and π orbitals. Evidence of the possible existence of this relationship is provided by the decrease in the intensity of the band on going from the cyclic 2,2-dimethyl-5-phenyl-1,3,2,5-dioxasilaphosphorinane (XVI) (9000 [94]) and the sterically unstrained compound (XIII) with X = Me (5550 [95,96]) to diethylphosphine (3920) and its dimesityl (1700) and di-t-butyl (1890) derivatives[95,96]. The decrease in the intensity of the R-band in phenyldialkylphosphines has been taken by many authors as proof that the compounds, in addition to the main conformer in which the n and π orbitals are orthogonal, also contain another conformer with geometry (ω = 0°) favourable for $n-\pi$ conjugation[95–97].

There are other viewpoints on the interpretation of the ultraviolet spectroscopic data. Some authors consider that when there is $p-\pi$ conjugation, the R-band should be absent, as observed for aniline derivatives[98–100]. It is suggested that the difference may be due to a difference between the energies of the orbitals of the UEP of the central atom and the π-orbitals of the benzene ring[101]; in aniline, the energy $E(n_N)$ is lower than $E(\pi)$, whereas in phenylphosphines (and phenylarsines), the order of the energies is the opposite [$E(n_P) > E(\pi)$], so that the $n \rightarrow \pi^*$ transition is observed in the ultraviolet spectra at long wavelengths.

The problem can apparently be solved by comparing the ultraviolet spectra of compounds whose three-dimensional structure has been studied. In the dialkyl phenylphosphonite series, the ultraviolet spectra have been characterised for the cyclic compound (XIV) with forced coplanar orientation of the n and π orbitals[101] and the acyclic diethyl phenylphosphonite $PhP(OEt)_2$ (XVII),[100] but there are no structural data for the latter. In the dialkylphenylphosphine R_2PPh series, no direct experimental results have been obtained on the structure of the cyclic analogue. Here, the ultraviolet spectra show an increase in the intensity of the R-band on going from the acyclic compounds ($\varepsilon \leq 5550$) to the cyclic compound (XVI) (ε = 9000).[94–96]



(XVI) (XVIII) (XIX), Y=O, S

The observed effect was attributed to the parallel orientation of the n_P and π orbitals in compound (XVI). A study of the three-dimensional structure of compound (XVI) using the Kerr effect did not make it possible to reach sufficiently definite conclusions about the orientation of the phenyl group[102]. Available data for the analogoues with P(IV) [for compounds (XVIII) [103] and (XIX) [104]], however, indicate a change in the conformation of α-Ph to the parallel conformation, compared with the corresponding 1,3,2-dioxaphosphorinanes, as a consequence of the fact that in these analogues there are no 1,3-synaxial interactions. In six-membered rings, the orientation of the plane of the benzene ring is determined primarily by steric effects[36], which are approximately the same in corresponding P(III) and P(IV) compounds. This indicates the need to obtain additional experimental data for systems of the 5-phenyl-1,3,5-dioxaphosphorinane type.

The above material on the structure and ultraviolet spectra show that it is as yet difficult to speak of the existence of a

direct relationship between the intensity and position of the R-band and the orientation of the n and π orbitals[101].

The electronic interactions in arylphosphines are analysed using the shielding parameters of the aromatic carbon atoms in ^{13}C NMR spectra[105-107]. The variation in these quantities on going from compounds (XIII) with X = H, Me to compounds with X = t-Bu is attributed[107,108] to conformational rearrangements; for compounds of the first type, in the opinion of the authors cited, there is free rotation of the phenyl group, whereas in the second case a conformation with orthogonal orientation of the n and π orbitals is produced.

The clearest picture of the magnitude and strength of the mesomeric interaction of a substituent X with a phenyl ring or an acetylenic bond can be obtained from the photoelectron spectra: the HOMO in phenylphosphines is formed by the interaction of the π-levels of benzene and the n_P orbital. The greater the splitting of the $b_1(n)$ and $b_1(\pi)$ orbitals from the photoelectron spectra, the greater the $n-\pi$ interaction. For compounds of the (XIII) series with X = Me,[100] X = Cl,[109] and X = OEt (XVII),[50,51] no significant splitting was detected. For phenylphosphine (X = H), the data obtained are not unambiguous[92,93,108-110], and they have been collected and examined with the introduction of data on other monophenylphosphines to refine the assignment of the bands in Ref.93; the splitting obtained (0.49 eV) indicates the existence of an interaction. It increases by a factor of 1.4 on going to t-butylethylphosphine[111]; for the corresponding chloro-derivatives, the splitting is much smaller[93,111].

An appreciable interaction of the phosphorus-containing group with the neighbouring π-electron system is indicated by an analysis of the photoelectron spectra of di-t-butylpheylphosphine and di-t-butylvinylphosphine[92]. The photoelectron spectra of the above compound (XVII), whose ultraviolet spectrum shows an R-band of medium intensity[100], have been discussed[50,51]. The second band in the spectrum of this compound is due to the ionisation of the π-electrons of the benzene ring. Its splitting into components corresponding to the orbitals $\pi(a_2)$ and $\pi(b_1)$ is slight, and is not recorded sufficiently clearly, but the components (9.22 eV and 9.40 eV) can be determined approximately[50,51]. The fact that the splitting of the π-orbitals is slight may indicate that their interaction with the UEP of the P(III) atom is slight. The experimental value of the ionisation potential of the n_P orbital obeys the additivity rule, and this is another indication that the mixing of the n_P and π orbitals is slight.

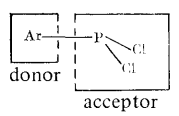
It follows from the above material on monophenylphosphines that the results obtained are often contradictory. The apparent reason is that the authors of almost all spectral studies assume that the π-orbitals of the benzene ring interact with the neighbouring fragment only in one form with $\omega = 0°$, when $n-\pi$ conjugation is possible. An orbital examination (see next section) shows, however, that structural conditions are created for another form of conjugation, of the $\pi-\pi^*$ type, which undoubtedly also influences the position and character of the bands in the spectra (see for example Ref.92). Since spectral studies make it possible to reach conclusions only about the strength of the effects of conjugation with the π-orbitals of the benzene ring, it is obviously necessary to solve the problem of the manifestation of both types of conjugation in the spectral characteristics and their relation to the three-dimensional structure.

3. THE NATURE OF THE ELECTRONIC INTERACTIONS IN PHENYLPHOSPHINES

Drawing an analogy between the electronic structure of amines and phosphines with phenyl substituents, many authors at first assumed that compounds of tervalent phosphorus, like nitrogen compounds, should be stabilised by $p-\pi$ conjugation effects. Analysis of a large amount of experimental data and the electronic state of the P atom, however, led Tsvetkov and Kabachnik[112] to the conclusion that conjugation is inhibited in arylphosphines; these results led to extensive discussion[113]. In spite of this, in spectroscopic studies the results obtained are often interpreted from the viewpoint of possible $n-\pi$ conjugation; these studies have been criticised[114]. Overall, the structural data obtained[82-89], together with spectral characteristics[94-97], lead to the conclusion that there is limited $n-\pi$ interaction. A recent combined study[115] of the integral intensities of the bands due to the CH vibrations in the infrared spectra, the $^1J(C, H)$ spin–spin coupling constants, and the rate constants for deuterium exchange in the Me group in phenylphosphines showed the absence of $n-\pi$ conjugation.

In a paper[92] on the photoelectron spectra of vinyl- and phenylphosphines, it was suggested for the first time that the predominant form of electronic interactions in these systems is not $n-\pi$ or $d_\pi-p_\pi$ conjugation, nor an inductive effect, but $\pi-\sigma^*_{P-C}$ hyperconjugation. A similar conclusion was later reached[89] from an analysis of the values of the long-range spin–spin coupling constants $^5J(C, H)$ and $^5J(C, F)$ and the barriers to internal rotation in dihalogeno-derivatives of phenylphosphines[89]. Delocalisation of electron density in the direction from the phenyl group to P is detected from a comparison of the chemical shifts of the ^{13}C NMR signals of the benzene ring[116]. An analysis of the dipole moments of aryldichlorophosphines by a vector-statistical method[83,117] showed a significant displacement of the π-electron density of the aryl group towards the P–Cl bonds: the polarity of the $C_{Ar}-P$ bond decreases considerably on going from aryldichlorophosphines (1.43 D) to triarylphosphines (0.38 D [31]), arylphosphines (0.07 D [117]), and 2-phenyl-1,3,2-dioxaphosphorinane (0.25 D [31]); the dipole moment of the P–Cl bond increases to 1.87 D (compared with 0.56 D in PCl_3). The displacement of electron density from the aryl group to phosphorus cannot be explained within the framework of the concept of $n-\pi$ conjugation.

The dependence of the type of orbital interactions in aryldichlorophosphines on the spatial orientation of the aryl group can be considered. The molecule can be broken down into two fragments; the first, the aryl group, is a π-electron donor, and the second, as a result of the antisymmetric combination of unoccupied orbitals of the P–Cl bonds, forms a low-lying $\pi^*_{PCl_2}$ orbital (XX).



(XX)

With the parallel orientation of the n_P and π orbitals (see Fig.1, $\omega = 0°$), steric conditions are created for $n-\pi$ conjugation, and with the perpendicular orientation ($\omega = 90°$) for $\pi-\pi^*_{PCl_2}$ interaction[118]. For X = H, the energy of the orbital $\pi^*_{PH_2}$ is high, and $n-\pi$ interaction is more effective. The energy of the orbital $\pi^*_{PX_2}$ is lowered considerably when the H atom is replaced by Alk and more particularly by Cl, which leads to stabilisation of the bisector conformation. It should be noted that in vinylphosphines, interactions with the π-system should be more clearly defined, since in the phenyl compound they are weakened as a result of delocalisation of the π-electrons.

The analysis carried out makes it possible to explain the factual material which has now accumulated on the three-dimensional and electronic structure of arylphosphines. It shows that the increase in the π-acceptor properties of P-containing groups compared with their N-analogues radically alters the nature of the predominant form of electronic interaction, which, as in 2-X-1,3,2-dioxaphosphorinanes (see section II), is not limited to the phosphorus atom, but extends further towards the whole acceptor group.

In conclusion it should be noted that for arylarsines, electron diffraction distributions analogous to those observed for phosphorus compounds have been detected[117,119]; these can be fully explained within the framework of the concept of intramolecular electronic interactions discussed here.

IV. ORBITAL INTERACTIONS IN COMPOUNDS OF FOUR-COORDINATE PHOSPHORUS

The properties of P(IV) compounds of the type $X^1X^2X^3P{=}Y$ are to a large extent determined by the P=Y group, where Y = O, S, Se. The variation detected by different physical methods in various parameters of the P=Y bond with change in the nature of the substituent X [4,120,121] indicates that a significant role is played by electronic interactions with the P=Y bond. An analysis of the factors influencing such a fundamental characteristic of the bond as the electron density distribution must eventually make it possible to reach specific conclusions about its electronic structure. It is appropriate to follow from this viewpoint the influence of structural factors on the polarity m(P=Y) of the P=Y bond. Linear relationships have been established between the phosphoryl group wavenumbers in the infrared spectra and its dipole moment[122,123]. An attempt has been made to derive a relationship between m(P=Y) and the sum of the constants $\Sigma\sigma_i$ for Y = O, S, Se.[124] Recent detailed studies of the polarity[16,120,124,125], basic nature[126,127], and ionisation potentials[15] of heterophosphoryl bonds and the three-dimensional structure as a whole[10] are revealing a number of new relationships and the nature of the orbital interactions.

1. THE POLARITY OF THE P=Y BOND

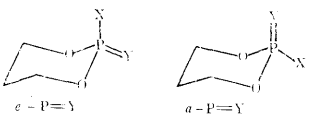
In symmetrically substituted compounds $X_3P{=}Y$, the polarity of the P=Y bond is estimated as the vector difference in the dipole moments of the P(III) and P(IV) compounds (for non-regular substituents X, rigidly fixed bicyclic structures are used).[16,125] Values have been obtained in this way for m(P=O), D:[16,37,125] C_3P (3.40) > N_3P (3.27) > Cl_3P (3.13) > O_3P (2.95); for m(P=S):[16,37,125] C_3P (3.88) > N_3P (3.19) > O_3P (2.62) > Cl_3P (2.03); and for m(P=Se):[124,128] C_3P (4.0) > N_3P (3.88) > O_3P (2.50). The observed increase in the range of variation in the values of m(P=Y) in the order Y = O, S, Se is apparently due to the increase in the polarisability of the P=Y bond (the total polarisability of the bond is b = 4.95 Å^3 for Y = O;[16] b = 13.64 Å^3 for Y = S;[16] and b = 17.63 Å^3 for Y = Se [129]). The effect is naturally more clearly defined for the easily polarised sulphur and selenium atoms.

The reasons for the change in the order of increase in the polarity of the P=Y bond in a series of compounds of the type $YP(OR)_3$; m(P=O) > m(P=S) > m(P=Se), and in the series of compounds YPR_3: m(P=O) < m(P=S) < m(P=Se), have been discussed[121]. According to photoelectron spectroscopic data, the formation of the P=Y bond is regarded as involving the σ-donor transfer of the UEP of the P(III) atom to an unoccupied orbital of the Y atom. The two unshared p-pairs of the Y atom are able to undergo a π-donor interaction of opposite sign with a molecular orbital of the PX_3 group, and this interaction is not limited to the central atom, and can extend in the direction of the atoms of the substituents X.[130]. Quantum-mechanical calculations by the CNDO/2 method also confirm the existence of a hyperconjugation interaction of degenerate orbitals n_Y with σ-bonding molecular orbitals of the P–X bonds[130]. In P(IV) compounds, the first ionisation potential corresponds mainly to the ionisation of the four p_π electrons of the Y atom, and it can serve as a measure of the back transfer of electron density[15]. For the compounds $X_3P{=}Y$ with Y = O, S, the ionisation potential decreases in the following order of substituents X_3:[15] Cl_3P > $(EtO)_3P$ > $(Me_2N)_3P$ > Me_3P. The polarity of the P=Y bond increases in the same order. This indicates the important role of delocalisation effects due to $n{-}\sigma$ hyperconjugation interaction in the production of the electronic structure of the P=Y bond, and as in the case of tervalent P compounds, this effect is greatest for P–Cl and P–O bonds[121].

The donor power of the p_π orbital of the UEP of the atoms O, S, Se, according to their ionisation potentials[15], increase in the order O < S < Se. It is increased in the reaction with low-lying UEP of neighbouring atoms (X = OR, Cl) and is decreased in interactions with high-lying pairs (X = NR_2). Thus in compounds of the type $R_3P{=}Y$ in which the donor power of the UEP and the acceptor power of the P–C bonds are lowered, delocalisation effects are shown to the smallest extent; the order of the increase in m(P=Y) corresponds to the order of the polarisability of the donor–acceptor bonds: (P → O) < (P → S) < (P → Se).

The degree of back transfer of the four p_π electrons from the heteroatom Y is greater, on the one hand, for compounds with X = Cl and OR, and on the other hand for compounds with Y = Se, and then Y = S and Y = O. The superposition of the delocalisation effect also leads to a change in the order of the increase in the dipole moment of the P=Y bond in the compounds $(RO)_3P{=}Y$ and $R_3P{=}Y$.

The influence of the nature of the substituent X on the polarity of the P=Y bond is revealed in a study of unsymmetrically substituted compounds of the 2-X-2-Y-1,3,2-dioxaphosphorinane type (XXI).[121,125] It also depends on the conformational characteristics, as was first pointed out in a study of the dipole moments of 2-methyl- and 2,4-dimethyl-2-thiono-1,3,2-dioxaphosphorinanes[16]: the a and e P=Y bonds have different polarities[121].



The greatest difference was found for the compounds with X = H: for the a and e P=O bonds, the values obtained were 3.25 D and 2.95 D;[121,132] for X = NR_2 the differences are 0.25 D (3.60 D and 3.33 D for the P=O bond[133], and 3.53 D and 3.33 D for the P=S bond[134]). The smallest difference was observed for phosphonates (X = Me), where for the a and e bonds, m(P=O) is 3.36 D and 3.33 D.[126,135]

For conformationally uniform compounds, only the polarity of the e P=Y bond has been determined; it is a minimum in chlorophosphates (X = Cl) [m(P=O) = 2.40 D and m(P=S) = 2.10 D [125]]; in phosphates (X = OMe) it increases to 2.95 D and 2.68 D respectively[125]; and in the phenoxy derivatives (X = OPh) it is slightly greater than in compounds with X = OR.[136] The polarity of the P=Y bond has been estimated graphically in 2-phenyl-1,3,2-dioxaphosphorinane oxide and sulphide; the values found were 3.0–3.5 D and

2.8 D respectively[31]. Quantum-mechanical calculations have also detected variation in the polarity of the phosphoryl group with change in the nature of the substituent X in compound (XXI),[127] but the high absolute values obtained have been criticised[121]. Thus the dipole moments of the P=Y bonds in 1,3,2-dioxaphosphorinanes evidently undergo appreciable changes with change in the nature of X (in the range 1.0–1.5 D) and with change in the orientation of the P=Y bond (~0.3–0.5 D).

2. BASIC NATURE OF THE PHOSPHORYL GROUP

Changes in the polarity of the P=Y bond are reflected in the variation in the physical and chemical properties of the compounds. For the phosphoryl group, these characteristics are the vibrational wavenumbers in the infrared spectra and the basic character. The order of the basic nature of 2-oxo-1,3,2-dioxaphosphorinanes, determined relative to $\Delta\nu_{OH}$ for phenol[127], correlates with the magnitude of the dipole moment of the phosphoryl bond, and changes in the following sequence of X (Fig.2):[121]

$$Cl < OPh \sim H \sim OMe < Ph < Me < NR_2.$$

The order obtained also reflects the regular features found above: for electron-acceptor substituents, $m(P{=}Y)$ and the basic nature of the phosphoryl group are smaller than those for electron-donor substituents. Here, as in the symmetrically substituted compounds, the influence of delocalisation is apparently being shown. Unfortunately, data on the photoelectron spectra of 2-oxo-1,3,2-dioxaphosphorinanes are extremely limited (only the first ionisation potentials have been obtained),[137] so that a correlation with delocalisation effects is not possible[121].

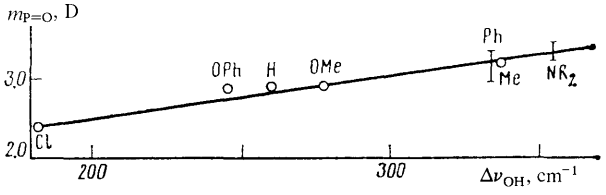
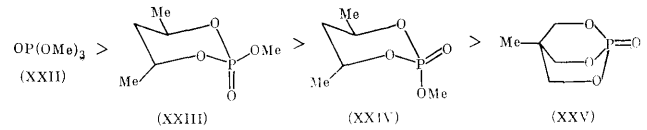


Figure 2. Correlation between the polarity and the order of basic nature of the phosphoryl group, determined relative to $\Delta\nu_{OH}$ for phenol[121].

In the discussion of the influence of the conformational characteristics on the basic nature and polarity of the P=Y bond, it is useful to compare the corresponding parameters of compounds with different three-dimensional structures and the same environment of the phosphorus atom. In 1,3,2-dioxaphosphorinanes, the more polar *a* P=Y bond should also be more basic. This order of basic nature of the phosphoryl oxygen atom was in fact established for the 2-hydro-2-oxo- and 2-methoxy-2-oxo-derivatives.[126] If however it is borne in mind that the *e*-orientation of the P=Y bond corresponds to the TT conformation of the P–O bonds, and the *a*-position to the GG′ conformation, it may be concluded that in the TT conformation, the degree of delocalisation of the p_π electrons of the Y atom is greater, and this leads to a decrease in the polarity of the P=Y bond[121].

An analogous relationship is revealed in the trialkyl phosphate series, for which the following order of decrease in the basic nature of the terminal oxygen atom was observed[126]:



The members of the series differ in their structural characteristics: for compound (XXII), the GGG conformation is preferred[138]; the second member of the series (XXIII) is characterised by equilibrium between the forms GGG ⇌ TGG′ (the conformation of the exocyclic group is given first);[139] the third member has the GTT conformation[139]; and the last member (XXV) has the TTT conformation[121]. As the T conformations accumulate, the effect of delocalisation increases, with a consequent decrease in the concentration of negative charge on the terminal oxygen atom and a corresponding decrease in its polarity and basic nature.

V. INFLUENCE OF PHOSPHORUS-CONTAINING GROUPS ON ELECTRONIC INTERACTIONS IN NEIGHBOURING FRAGMENTS (O-PHOSPHORYLATED PHENOLS)

Phosphorus-containing groups have such a marked ability to take part in different types of electronic interaction that they can also change the nature of the mutual influence of atoms in fragments adjoining them. An example is provided by O-phosphorylated phenols, for which a fairly large amount of factual material has been accumulated. They contain the fragment P–O–Ar. In organic compounds of this type, the anisoles R–O–Ar, $p-\pi$ conjugation between the oxygen atom and Ar predominates, leading to stabilisation of the conformations with the parallel arrangement of the *p* and π orbitals[140] and to transfer of electron density from the oxygen atom towards the benzene ring[141,142]. Extensive studies have also been carried out for anisoles in which, as a consequence of steric strain, inhibition of $p-\pi$ conjugation is observed[143–147], revealed by reversal of the sign of the dipole moment of the C_{sp^2}–O bond, which changes from −0.39 D in anisoles to 0.05 D in its sterically hindered analogues[144].

In O-phosphorylated phenols, the group joined to the Ar–O group is a strong competing π-electron acceptor, namely the phosphorus-containing group. The question of whether it is capable of inhibiting $p-\pi$ conjugation, and which of the effects is stronger, $p-\pi$ conjugation or π-electron-acceptor interaction, can be considered. The view is held that the introduction into anisoles of a second unsaturated group capable of conjugation does not inhibit conjugation, since it may involve both unshared *p*- and sp^2-pairs of electrons of the oxygen atom[142,148], whose energy difference is small[142]. Other data show, however, that the presence of two π-electron systems on an oxygen atom in the molecule of an organic compound weakens its conjugation with each system separately[141,143]. For the analogous silicon compounds, it is suggested that both UEP are involved in conjugation with the phenyl group and the group containing the heteroatom[52]. This interaction should lead to an appreciable decrease in the electron density on the oxygen atom. The competition between these two types of interaction facilitates the production of the one which is energetically more favourable. This should be reflected primarily in the three-dimensional structure of the compounds: for $p-\pi$ conjugation, the more favourable structure is that in which the plane of the benzene ring coincides with the plane of the C_{sp^2}–O–E bonds, and the *p* and π orbitals are coplanar (Fig.3, $\alpha = 0°$); in the alternative conformation, the planes being considered are

mutually orthogonal ($\alpha = 90°$), and the sp^2 orbital of the UEP is in the same plane as the phenyl π-electrons.

The available data on compounds containing the fragment Ar–O–P(III) or Ar–O–P(IV) can be considered in turn.

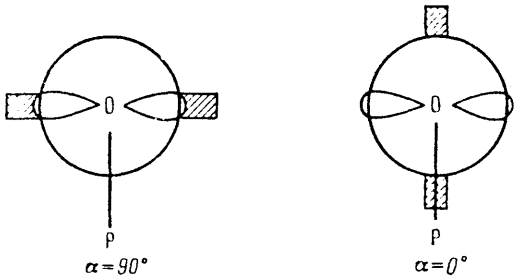


Figure 3. Boundary conformations of the benzene ring in O-phosphorylated phenols.

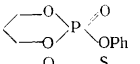
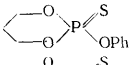
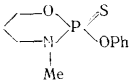
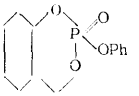
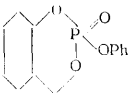
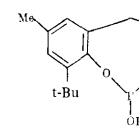
1. EXPERIMENTALLY MEASURED CHARACTERISTICS OF THE COMPOUNDS

a) Three-dimensional Structure of the Compounds

Within the framework of existing ideas, $p-\pi$ conjugation is energetically more favourable than $p_\pi-d_\pi$ conjugation, so that the production of conformations with parallel orientation of the p and π orbitals being considered is to be expected (Fig.3, $\alpha = 0°$). The results of most studies carried out up to the present, however, indicate the reverse: many types of phosphorus compound have a structure with an arrangement of the p orbital of the UEP and the π orbital of the benzene ring close to orthogonal (see later, Table 4). This orientation of the phenyl plane has been established by X-ray diffraction for phenoxythiophosphoryl hydrazide (XXXII), $\alpha = 87.2°$;[149] 2-phenoxy-2-thiono-5,5-dimethyl-1,3,2-dioxaphosphorinane (XXVII), $\alpha = 84.2°$;[150] 1,8-naphthalene phenyl phosphite (XXXI) [151] and the eight-membered 2-phenoxy-4,5,7,8-dibenzo-6H-1,3,2-dioxaphosphocine (XXXIII), $\alpha = 75.5°$.[152] In solution, 1,3,2-dioxaphosphorinanes retain the conformation characteristic of the crystalline state[136]; an analogous structure is shown by the phosphoryl analogue[136] and aryloxy-derivatives of tervalent phosphorus compounds[30]. The orthogonal orientation has also been established for pyrocatechol aryl phosphites[153]. According to NMR data, phenyl dichlorophosphate also has an appreciably non-planar structure[154]. The introduction of substituents in the p-position of the benzene ring in 2-aryloxy-1,3,2-dioxaphosphorinanes does not influence the angle of rotation of the aryl plane, indicating indirectly the absence of conjugation.

The orthogonal orientation of the p and π orbitals found for O-phosphorylated phenols is possibly not the exception but the rule for compounds containing elements of period III next to an aryloxy fragment. Thus phenyl silyl ether[155] and trichloro- and trimethylphenoxysilanes[156] have a structure close to orthogonal, and sulphur compounds, namely the aryl esters of arylsulphonic acids, also show appreciable non-coplanarity ($\alpha \cong 90 \pm 20°$).[157]

Table 4. P–O and C_{sp^2}–O bond lengths in O-phosphorylated phenols.

No.	Compound	Position	Bond length, Å				Refs.
			P–O (Alk)	P–O (Ar) *	C–O (Alk)	C–O (Ar)	
(XXVI)		*a*	1.565	1.59	—	1.41	[163]
(XXVII)		*a*	1.575	1.594	—	1.410	[150]
(XXVIII)		*a*	1.576	1.605	—	—	[164]
(XXIX)		*a*	1.579	1.575 (r); 1.571 (e)	—	1.409	[165]
(XXX)		*a*	1.586	1.565	1.47	1.409	[166]
(XXXI)	$C_{10}H_6O_2POPh$	*a*	—	1.626 (r); 1.656 (e)	—	1.412	[154]
(XXXII)		*a*	—	1.642 (r); 1.618 (e)	—	1.408	[152]
(XXXIII)	Ph (CH_2O) P (S) $OC_6H_2Cl_2Br$	—	1.579	1.615	1.420	1.394	[167]
(XXXIV)	$(H_2N-NH)_2$ P (S)OPh	—	1.609	—	—	1.415	[139]
(XXXV)	MeOPh	—	—	—	1.423	1.361	[160]
(XXXVI)	*p*-$MeOC_6Me_4OMe$	—	—	—	1.47	1.38	[161]

*Here, r = ring, and e = exocyclic P–O bond.

b) Electron Density Distribution

To establish the mechanism of intramolecular electronic interactions, it is of value to analyse the polarity of the C_{sp^2}–O and P–O bonds of the Ph–O–P fragment. The high electronic lability of the C_{sp^2}–O bond in anisoles was noted above (range of change in the dipole moment from −0.39 D to 0.05 D [144]). Diphenyl ether also shows a reversal of the sign of the dipole moment of the bond compared with anisole; the moment is directed towards the oxygen atom[141]. The chemical shifts of the signals in the ^{13}C NMR spectra in various substituted phenols also confirm that variation in the polarity of the C_{sp^2}–O bond over a wide range, depending on the nature and position of the substituents in the benzene ring[158]. The polarity of the P–O bond also varies over a fairly wide range with change in the type of substituent on the phosphorus atom[16]. All these data indicate that the π-donor or π-acceptor transfer of electron density at the oxygen atom is reflected in the change in the dipole moments of the bonds.

Data have now been obtained on the polarity of the C_{sp^2}–O bond in the following phosphorus compounds: triphenyl phosphite[159], pyrocatechol phosphites[153], and 2-aryloxy-1,3,2-dioxaphosphorinanes[30]. In all cases the dipole moment of the C_{sp^2}–O bond (0.3–0.8 D) is directed towards the oxygen atom; this indicates inhibition of $p-\pi$ conjugation. The σ-acceptor transfer of electron density in the direction of the oxygen atom is of comparable magnitude to the π-donor transfer, and predominates in these systems.

The second fragment, that is the P–O bond, can now be considered. In symmetrically substituted trialkyl phosphites, the polarity of this bond is zero[16]. In 2-X-1,3,2-dioxaphosphorinanes, the magnitude and direction of the dipole moment of the bond change with change in the nature of the substituent X (see Table 1),[16,59] and in the aryloxy-derivatives (X = OAr) the ring and exocyclic P–O bonds are non-equivalent and have different polarities[30]: the former have a dipole moment of 0.8 D, directed towards the phosphorus atom, whereas the dipole moment of the second atom is 0.22 D and is directed towards the oxygen atom, that is overall, electron density is transferred from the ring oxygen atoms towards the exocyclic P–O bond, which has clearly defined electron-acceptor properties. The transfer is analogous to that observed in 2-chloro-1,3,2-dioxaphosphorinane, where the P–Cl bond acts as acceptor[16]. σ-Acceptor transfer of electron density towards the oxygen atom also follows from an analysis of the dipole moments of pyrocatechol phosphites[153].

The data obtained from dipole moments on the polarity of the P–O bond in the P–O–Ph fragment exclude the possibility of π-acceptor interaction of the UEP of the oxygen atom with the phosphorus-containing group (p_π–d_π conjugation or hyperconjugation). In all the examples studied, the P–O–Ph fragment behaves as an electron density acceptor.

c) Bond Lengths

The additional bonding produced as a result of the conjugation effect (including p–π and p_π–d_π conjugation) is reflected in changes in the bond lengths. Increase in the length of a bond indicates a decrease in its double bond character and an increase in its antibonding character. For example, the C–O(Ph) bond length increases from 1.361 Å in anisole (XXXV) [160] to 1.38 Å in the sterically strained compound (XXXVI),[161] in which the methoxy groups are displaced from the plane of the benzene ring. In *p*-fluoroanisole, theoretical calculations have established an increase in the length of the C–O(Ph) bond by 0.014 Å on going from the planar to the orthogonal structure[162]. Table 4 gives the results of an X-ray diffraction study of the bond lengths in O-phosphorylated phenols. In all cases, an increase (by 0.03–0.05 Å) is observed in the C–O(Ph) bond length, indicating a decrease in its double-bond character compared with anisole and even with its sterically strained analogues.

The characteristics of phosphorus–ether bonds can also change with change in the type of intramolecular electronic interactions. The data in Table 4 show that in most cases [except compound (XXX)], the bonds next to Ar are longer than the P–O(Alk) bond, indicating that there is no additional bonding in the P–O(Ar) fragment. Thus this fragment has greater acceptor character than the P–O(Alk) group. For all the cyclic compounds given (XXVI)–(XXXII), the endo- and exocyclic P–O bonds are non-equivalent. In 1,3,2-dioxaphosphorinanes with a phenoxy group in the axial position, (XXVI)–(XXIX) and (XXXI), the increase in the antibonding character of the exocyclic bond is greater, and the bond is 0.02–0.03 Å longer than the ring bonds.

This effect is not related to a change in the nature of the substituent (Alk or Ar) on the O atom, since it is also observed in the compounds (XXXI) and (XXXII),[151,152] although in the last case the increase in the antibonding character of the P–O(Ar) bond is greater. This difference is related to the conformational characteristics of the bonds: in 1,3,2-dioxaphosphocine[152] and also in the bicyclic *trans*-isomer of 1,3,2-dioxaphosphorinane (XXX),[166] the exocyclic P–O(Ph) bonds occupy the *e* position, in contrast to all other compounds, where this bond is in the axial position. For the *e* position there is a change in the three-dimensional structure of the entire P–O–Ph fragment; from the "*cis*" conformation characteristic of the *a*-phenoxyl group,[30,136,150,151,163] the phenyl group changes to the T structure relative to the UEP of the P atom[152]; 1,3-synaxial interactions do not prevent the production of the T conformation. Change in the confirmations also leads to a change in the bond lengths: the conformations of the ring and exocyclic P–O bonds in compounds with the OPh group are described by the TTC [or TTG for P(IV)] structure, and with the *e* group by the GG'T structure. In all the examples given in Table 4, an increase in length is observed for the bonds characterised by the T conformation.

d) Photoelectron Spectra

Unfortunately, almost no studies have been carried out for compounds containing the P–O–Ph fragment. The photoelectron spectra of phenyl dichlorophosphate have been published[168]; splitting of the $\pi(b_1)$ and $\pi(a_2)$ orbitals of the benzene ring was not detected, and this may indicate that there is no p–π conjugation.

e) ^{13}C NMR Spectra

The π-electron density distribution in derivatives of phenol and anisole can also be estimated from the chemical shifts in the ^{13}C NMR spectra;[142,169,170] here, the changes in the chemical shifts of the carbon atom in the *para*-position of the benzene ring are due to the effect of conjugation. In alkyl phenyl ethers, with inhibition of p–π conjugation, a decrease in the shielding of C_n compared with anisole was detected[145,158,170]. According to published data, in O-phosphorylated phenols[171,172] and anilines[173] the deshielding of the C_n atom increases and reaches 2.7–6.3 p.p.m. The weak-field displacements of the C_n signal in phosphorus compounds (by analogy with systems in which steric inhibition of the p–π conjugation effect is observed) can be attributed to a decrease in or even the absence of interaction between the p orbitals of the oxygen atom and the π orbitals of the benzene ring.

f) Ultraviolet Spectra

The participation of the π-electron of the benzene ring in conjugation with the UEP of the oxygen atom can be studied from the ultraviolet spectra; it is revealed in a bathochromic shift and an increase in the intensity of the λ_2 and λ_1 absorption bands of benzene (in anisole, 217 nm, ε = 8050; 271 nm, ε = 1500 [140]). In t-butyl phenyl ether and 2,6-dimethylanisole, where conjugation is sterically inhibited, the intensity of the λ_3 band is low (460,[174] 334 [146]).

The ultraviolet spectra of derivatives of 2-phenoxy-1,3,2-dioxaphosphorinanes have been studied[172].

For the 2-oxide and the 2-sulphide, a complete analogy with the spectra of the sterically strained anisoles is observed: the λ_2 band does not undergo the bathochromic shift characteristic of anisole, the fine vibrational structure of the λ_3 band is preserved, and its intensity does not exceed 440. The general form and position of the λ_3 band are also preserved for the compound with P(III), ε_{max} = 520. The analysis of the λ_2 band is made difficult by the presence of

additional absorption in the region of ~200 nm, due to the $n-\sigma^*$ transfer of the UEP of the P(III) atom[172,175]. The preservation of the autonomous organisation of the benzene ring in 2-phenoxy-1,3,2-dioxaphosphorinanes indicates that $p-\pi$ conjugation is inhibited in these compounds. Additional analysis of *p*-bromo- and *p*-alkyl-substituted dioxaphosphorinanes indicates that the O-phosphorylated group has electron-acceptor properties[172].

g) Reactivity

The study of the ionisation constants and reactivity of pyrocatechol phosphites and other cyclic systems containing the P–O–Ph fragment indicates an increase in the acceptor properties of these groups, compared with the analogous systems in which the phenyl group is replaced by an alkyl group[176,177]. A fundamental difference has been detected in the distribution of the products of the nitration of acetyl and phosphorylated derivatives of aniline and phenol; in the organophosphorus compounds, nitration takes place more rapidly in the *m*-position, and not in the *o*- and *p*-positions, as in the derivatives of aniline and phenol[178]. The authors cited[178] consider that this difference cannot be explained on the basis of existing ideas about the effects of substituents. Data on the dual behaviour of the oxygen atom, depending on the nature of the substituents round it, make it possible to attribute the preferential formation of the *m*-products in the nitration of O- and N-phosphorylated phenols and anilines to the acceptor properties of the oxygen atom in these systems.

2. THEORETICAL EXAMINATION

The above experimental data show that fairly extensive material has now accumulated on the three-dimensional and electronic structure of O-phosphorylated phenols and their chemical behaviour, indicating that the phosphorus-containing group has a specific influence on the nature of the interaction between the phenyl group and a neighbouring oxygen atom on the one hand, and the oxygen atom and the phosphorus-containing group on the other. The data obtained, that is the approximately orthogonal orientation of the π-orbitals of the benzene ring and the *p*-orbitals of the UEP of the oxygen atom, the change in the direction of the dipole moment of the C_{sp^2}–O(P) bond compared with anisole, the preservation of the autonomous organisation of the absorption bands of the benzene ring in the ultraviolet spectra, and the increase in the acceptor properties of the P–O–Ph fragment compared with P–O–Alk, show that the predominant properties are not the π-donor properties usually observed for organic oxygen compounds, but σ-acceptor properties. In the O–C_{sp^2}(Ph) fragment, $p-\pi$ conjugation is inhibited, and in the P–O(Ar) group the signs of π-acceptor interaction are poorly defined. The dual behaviour of the O atom is due to the difference in the electronic structure of the substituents on it[179].

A theoretical examination by the non-empirical SCF method has shown that the σ-acceptor power of the oxygen atom is increased if the neighbouring fragment has a low-lying lowest unoccupied molecular orbital LUMO.[179] These properties are characteristic of the bonds formed by the phosphorus atom. According to the photoelectron spectra, their ionisation potentials are lower than the ionisation potentials of ether bonds[15]. This indicates an increase in the energy of the σ-occupied molecular orbitals, and probably a corresponding decrease in the energy of the LUMO.

The difference in the strength of the manifestation of the effect for P(III) and P(IV) compounds is also explained on the basis of these concepts. The bonds in the P(IV) compounds are more stable, as revealed by the fact that the P^{IV}–X bonds are shorter than the P^{III}–X bonds, and is detected thermochemically[5]. As noted above, the additional increase in the antibonding character of the bonds in the P(III) compounds is due to the α-effect. The increase in the antibonding character leads to a decrease in the energy of the σ-orbitals of the bonds and an increase in the strength of the manifestation of the π-acceptor properties of the O atom.

The dependence of the effect on the spatial characteristics was noted above. For P–O bonds, the greatest increase in antibonding character is observed in the T conformation (section II), in which the *p*-orbital of the UEP of the neighbouring oxygen atom is close to the T-position relative to the P–O bond, so that steric conditions are created for $n_O-\sigma^*_{P-O}$ interaction. This approach makes it possible to explain the non-equivalence of the P–O bonds in cyclic aryl phosphites (Table 4). The interaction affects the whole O_2POAr group, and is so effective that it is able to block the $p-\pi$ conjugation between O and Ar.

The additional compensation may be related to $\pi-\sigma^*$ interaction, so characteristic of benzyl halides[180–185], methylallylsilanes[186], and benzylphosphines[92]. A necessary condition for this interaction is the mutually perpendicular arrangement of the plane of the benzene ring and the σ-bond.[184,185] Fig. 3 shows that it is also fulfilled for O-phosphorylated phenols. An analysis of 2-phenoxy-1,3,2-dioxaphosphorinanes[30,172] shows that the picture of the electron density distribution in these compounds is consistent with this interaction: electron density is transferred from the phenyl group towards the oxygen atom.

Thus the introduction of a phosphorus atom next to an aryloxy fragment radically alters the nature of the orbital interactions of the central oxygen atom with neighbouring fragments, one of which contains π-electrons (the benzene ring), while the other is a strong π-acceptor (the phosphorus-containing group). The inhibition of $p-\pi$ and $p_\pi-d_\pi$ conjugation and the change in the nature of the electron density distribution and chemical reactivity of the compounds indicates that the predominant properties in these systems are not the usual π-donor but the σ-acceptor properties of the oxygen atom, due to the proximity to a low-lying unoccupied molecular orbital of the phosphorus-containing group of atoms.

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A systematic combined examination of the spatial and electronic characteristics of P(III) and P(IV) bonds has revealed the exceptional importance of many types of specific orbital interactions with low-lying unoccupied π^* and σ^* orbitals of the phosphorus bonds. It was previously assumed that these interactions did not take place or played an insignificant role in organic compounds. In recent years, the position has changed. Analysis of the conformational behaviour of a number of organic molecules has shown that these interactions play an important role in determining the three-dimensional structure of molecules of this kind[1,2]. Even for butadiene, which has become the classical example of a compound in which $\pi-\pi$ conjugation predominates, recent non-empirical calculations have shown that the energy of conjugation in the planar form is only slightly (~1.5 kcal $mole^{-1}$)

greater than the energy of hyperconjugation in the perpendicular conformation[187]. In phosphorus compounds, the acceptor power of the bonds is much greater, as a consequence of the decrease in the energy of the π^* or σ^* orbitals. Unfortunately, there are no accurate quantitative data.

The CNDO/S method has been used to estimate the energy of the π^* orbitals of the PX_2 fragment in vinylphosphine oxides. It amounts to 0.82 eV for X = F, −0.80 eV for X = Cl, and 2.34 eV for X = OMe; on going to the corresponding methyl derivative, the energy increases sharply to 6.0 eV.[188] Indirect confirmation of the marked decrease in the energy of the unoccupied orbitals of the bonds compared with organic compounds is provided by the decrease in the ionisation potentials of the phosphorus bonds, which indicates an increase in the energy of the occupied MO and apparently a corresponding decrease in the energy of the LUMO. The increase in the acceptor power of the P bonds compared with N is not an exception, and is characteristic of all elements of period III. It is a maximum in P(III) compounds as a consequence of the destabilising effect of the repulsion of the UEP of adjacent heteroatoms. The reasons for the decrease in the acceptor properties of P(IV) bonds compared with P(III) were noted above.

All the above material reveals the close relationship between the effects of the mutual influence of atoms and the three-dimensional structure of organophosphorus compounds. The nature of orbital effects is closely related to the conformational characteristics of the interacting orbitals: the effect of $n-\sigma^*$ hyperconjugation predominates for the *trans*-orientation of the orbital of the UEP and the σ-polar bond, whose acceptor properties are a maximum with the destabilising $n-n$ repulsion of the UEP of the adjacent heteroatoms forming this bond (the α-effect); $\pi-\sigma^*$ interaction in $ArPX_2$ becomes decisive with the parallel orientation of the π-orbitals of the benzene ring and $\pi^*_{PX_2}$, leading to the production of the bisector form. The same structural restrictions are revealed in P–O–Ar systems. From the last example it can be seen that the introduction of a phosphorus atom into organic compounds leads to changes in the nature of the electronic interactions not only in the groups directly adjoining this atom, but also in neighbouring fragments.

Comparison of the physical properties of compounds with their three-dimensional structure makes it possible to take a fresh look at the nature of the orbital interactions. Traditional theoretical ideas often not only cannot predict but even cannot explain the observed changes in various properties of the bonds in OPC. The present review presents clear proof that so-called "non-specific" electronic interactions often predominate. In the opinion of the present author, they can be called non-specific only in relation to organic compounds; as far as OPC are concerned, they are typical. For example, the above model of the destabilisation of the σ-bond in the T-position to the p orbital of the UEP of a heteroatom ($n-\sigma^*$ interaction) is being used increasingly to explain the reactivity of organic[189] and organophosphorus[18,190–192] compounds.

The present review gives the available experimental data for phosphorus compounds. Many of the above characteristic features, however, are also observed for the compounds of other elements of periods III and IV.[52–56] Thus for aryloxy-derivatives of S and Si, as for O-phosphorylated phenols, stabilisation of the structure with the orthogonal orientation of the p and π orbitals has been detected[155–157], and it has been reported[193] that there is no $p_\pi-d_\pi$ conjugation between the Si and O atoms in these systems. The combined study of the compounds by different physical methods, together with an analysis of the spatial characteristics, will make it possible to find a final theoretical basis for the observed phenomena.

An attempt has been made above to classify the observed effects from the viewpoint of perturbation theory. The problem examined requires a penetrating theoretical description at a higher level. There are grounds for hoping that the use of non-empirical methods of calculation will make an important contribution to the elucidation of the characteristic features of intramolecular electronic interactions in OPC. Moreover, there have as yet been few rigorous experimental studies to establish the nature, mechanism, and spatial-directed character of the effects of the mutual influence of atoms in phosphorus compounds (this applies particularly to photoelectron and X-ray spectroscopic studies).

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