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Conjugation in the Series of Phosphorus(III) Compounds

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In its electronic effect phosphorus(III) is usually regarded as an analogue of tervalent nitrogen. However, in recent years it has been shown that substituents with phosphorus(III) do not exhibit a π-donor effect, which is characteristic to a greater or smaller extent of groups containing the elements in Periods II and III with lone pairs of electrons. On the other hand, substituents with phosphorus(III) exhibit a π-acceptor effect, characteristic of *meta*-orienting groups, and probably due to the interaction with the vacant orbitals of phosphorus. Thus, in contrast to elements of Periods II and III with lone electron pairs, phosphorus(III) is incapable of $p-\pi$ conjugation. The absence of the capacity of the lone electron pair of phosphorus to undergo delocalisation (or the presence of only insignificant capacity of this kind) has been explained by an enhanced *s*-character of the lone pair orbital, which is confirmed by data for the valence angles in phosphorus(III) compounds. The physical and chemical properties of phosphorus(III) compounds in which there is a possibility of $p-\pi$ conjugation are discussed in the review from this standpoint. All the properties are consistent with the hypothesis of the predominant *s*-character of the lone electron pair of phosphorus.
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I. INTRODUCTION

The development of the chemistry of organophosphorus compounds is to a considerable degree due to phosphorus(III) compounds, which, by virtue of their high reactivity, occupy an outstanding place among other types of organophosphorus derivatives. The most interesting reactions of phosphorus(III) compounds are accompanied by an increase in valence and the involvement of the lone pair in the formation of a new bond. Thus the properties of phosphorus(III) compounds associated with the participation of the lone pair in intermolecular electronic steps have been widely investigated. Nevertheless little is known about the nature of the lone electron pair of phosphorus and its intramolecular interactions with attached π-electronic systems. Phosphorus in the tervalent state is perhaps the only element in the Second and Third Period forming organic derivatives about the electronic effect of which there has been virtually no information until recently. By analogy with nitrogen and other elements with lone electron pairs and also according to its position in the Periodic System, it was usually postulated[1,2] that it should be an *ortho–para* directing substituent with a highly pronounced π-donor conjugation effect.

According to the classical concepts developed by the English School of Chemistry[3] the capacity of the lone electron pair of any atom for $p-\pi$ conjugation is associated with the position of the element in the Periodic System. Thus, within the limits of a single Period, it decreases from left to right and within the limits of a single Group from above downwards:

$$R_2N > RO > F;\ F > Cl > Br > I;\ RO > RS\ .$$

Later these qualitative relations were confirmed on the quantitative scale of resonance effects proposed by Taft[4,5].

Using these relations, one may expect that the effect of π-donor conjugation of substituents with phosphorus(III) will be greatest among the elements of the Third Period:

$$R_2P > RS > Cl$$

Compared with nitrogen, the effect should be only slightly reduced, to the same extent as on transition from oxygen to sulphur. Apart from π-donor conjugation, a π-acceptor d-orbital interaction effect, which is probably characteristic of all the elements in the Third Period but is shown in a pure form only in the case of silicon, can also be postulated for phosphorus(III). However, on the whole these comparisons might have led to the expectation that substituents with phosphorus(III) would be *ortho–para* directing and would exhibit a positive mesomeric effect.

However, the study of the chemical properties of phosphorus(III) compounds showed that, contrary to the above considerations, phosphorus is greatly inferior in its capacity for $p-\pi$ conjugation not only to nitrogen but even to sulphur and chlorine. Moreover, so far no property has been found involving a distinct effect of the capacity of the lone electron pair of phosphorus for $p-\pi$ conjugation in the ground state of the molecule. Therefore the above series should be reformulated as follows:

$$RS > Cl > R_2P\ .$$

Owing to the absence or insignificance of the π-donor effect, phosphorus(III) exhibits distinct π-acceptor properties, probably via $p_\pi - d_\pi$ conjugation and therefore belongs to *meta*-directing groups. Chemically this was demonstrated for the first time by the authors of the review together with Chang Jung-yu in experiments on the directive influence in the addition of secondary amines to vinyl derivatives of phosphorus(III).[6-8] Subsequently these conclusions were confirmed and developed by the present authors with other collaborators[9-15] and in a number of studies in the Soviet Union[16,17] and abroad[18-40].

In order to account for the unusual properties of phosphorus(III), we put forward a hypothesis together with Bochvar and Lobanov[9,11,12] according to which the reason for the lack of capacity for (or low tendency towards) $p-\pi$ conjugation of the lone electron pair of phosphorus(III) is due to the type of hybridisation of its orbital or more precisely its enhanced s character, which was confirmed by data on the geometry of phosphorus(III) compounds.

In the present review an attempt is made to examine consecutively from the standpoint of this hypothesis the physical and chemical properties of phosphorus(III) compounds in which an effect of $p-\pi$ conjugation is possible. In the first place much attention has been devoted to the structure of the electronic shell of phosphorus(III) and the geometry of its compounds. Next the physical and chemical properties associated with the lone electron pair of phosphorus in both ground and optically excited states are considered on the basis of these data.

We believe that such treatment is particularly necessary, since the view that phosphorus(III) is a complete analogue of nitrogen, which exhibits π-donor properties in aromatic and unsaturated compounds, has become firmly rooted in the literature. This view is sometimes encountered in monographs[1,2] without serious experimental justification. The problem of $p-\pi$ conjugation in phosphorus(III) compounds was partly dealt with in a recent monograph by Hudson[41] which has been translated into Russian. However, these problems are treated from traditional standpoints and the latest data which contradict the view expounded are not discussed.

II. THE STRUCTURE OF THE ELECTRONIC SHELL OF TRICOORDINATE PHOSPHORUS

A. GROUND STATE

The electronic shell of the neutral phosphorus atom contains 15 electrons. Ten of these are in the first and second quantum levels K and L ($1s^2 2s^2 2p^6$) and five occupy the s and p orbitals of the M valence shell ($3s^2 3p^3$). The latter has a further five unfilled d orbitals; the $3s$ and $3p$ orbitals do not differ in symmetry from the $2s$ and $2p$ orbitals but are more diffuse. The p orbitals are symmetrical relative to the three coordinate axes.

The symmetry of the d orbitals is more complex. Their distribution in space is shown in Fig. 1, where each of the five d orbitals is presented separately, and also in Fig. 2, where a steric model of superimposed d orbitals is shown. In the isolated atom all the d orbitals are energetically equivalent (degenerate). Under the influence of the electric fields of adjacent atoms, the energy levels of the d orbitals are split into two groups: d_γ orbitals (d_{z^2} and $d_{x^2-y^2}$) directed along the coordinate axes and having lower energies, and d_ϵ orbitals (d_{xy}, d_{xz}, and d_{yz}), which have maxima at 45° to the coordinate axes. Apart from the s and p orbitals, the d_γ orbitals (sp^3d and sp^3d^2 hybridisations) are usually employed in the formation of σ bonds. The d_ϵ orbitals probably participate in the formation of $p_\pi - d_\pi$ bonds.

The energy difference between the $3s$ and $3p$ orbitals of phosphorus is less than between the $2s$ and $2p$ orbitals of

nitrogen[41] (Fig. 3). The valence shell of the latter also consists of five electrons ($2s^2 2p^3$), but, in contrast to phosphorus, it does not have d orbitals in the same quantum level. Therefore the transition of the valence electrons of nitrogen to the d orbital (for example $2s \rightarrow 3d$) is coupled with a greater energy expenditure (about 530 kcal mole^{-1}) than the analogous transition of phosphorus electrons ($3s \rightarrow 3d$, 380 kcal mole^{-1}). It appears that in many ways this difference is responsible for the specific features of phosphorus chemistry. Possibly other higher phosphorus levels (4s, 4p) also have an effect. The energy levels of the electronic configurations of the unionised phosphorus atom (based on spectroscopic data) are quoted in van Wazer's book[42].

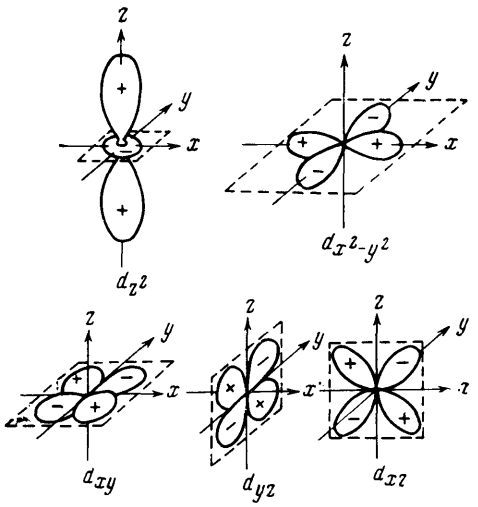


Figure 1. The form and relative orientations in space of d orbitals[359].

B. VALENCE STATE

The valence state of phosphorus(III), i.e. the state of the electrons of its valence shell on formation of three σ bonds, naturally differs from the ground state. According to the quantum-mechanical theory of valence[43,45] in its simplest form, when bonds are formed by any atom, for example phosphorus, nitrogen, oxygen, or sulphur, p orbitals are employed, since they give rise to stronger bonds than s orbitals (the strength is 1 for the 2s orbital and 1.732 for the 2p orbital). Accordingly, the angles in the compounds of the above elements, for example in hydrides, should be 90°. Indeed, in the case of the hydrides of phosphorus, sulphur, and higher analogues the valence angles only slightly exceed 90° (Table 1). However, ammonia and water have almost tetrahedral valence angles. The increase of the valence angle, even if only slight, is evidence of a deviation of the valence state from the ground state.

The orientation of bonds in a particular direction in space is explained in valence theory by the directed orientation of p and d orbitals. Geometry inconsistent with their configurations is regarded as a result of hybridisation with other orbitals, in particular s orbitals. The hybrid $s-p$ orbitals form stronger bonds than the pure p orbital (the strength for the sp^3 orbital is 2) and therefore the tetrahedral configuration is the most favourable from this point of view. However, the tendency for molecules with lone pairs of electrons to form a tetrahedral configuration is counteracted by the opposing tendency to retain the lone s electron pair, since the latter has the lowest energy. As a result, the valence angle assumes an intermediate value between the right angle and the tetrahedral angle. The above considerations do not of course explain the differences in the geometries of the molecules in the Second and Third Periods. The reasons for these differences in valence angles are much more complex.

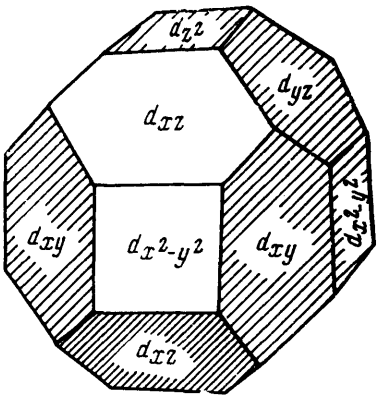


Figure 2. A steric model of superimposed d orbitals[360].

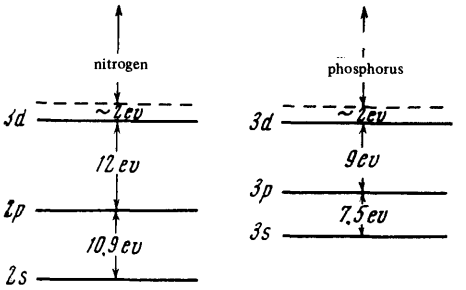


Figure 3. Atomic energy levels of nitrogen and phosphorus[41].

At the present time there exist two approaches to this problem, according to one of which, based on valence theory, the main reason for the increase of valence angles is the Coulombic repulsion of the atoms linked to the central element. This hypothesis was put forward for the first time by Pauling[43,44]. Subsequently the Coulombic and exchange repulsion of bonding electrons was also taken into account.[45] These factors should play a smaller role in the case of central atoms with large radii and therefore the repulsion and correspondingly the valence angles should be greater for compounds of elements of the Second

Period. Mulliken[54] calculated the repulsion energy of hydrogen atoms in the phosphine molecule and showed that, owing to the large radius of the phosphorus atom, it is smaller by a factor of approximately 3 than for ammonia (the N–H and P–H bond lengths are respectively 1.014 and 1.414 Å). Even when the valence angle in PH_3 is altered to 90° and in NH_3 to 120°, the repulsion energy in the first case is smaller by a factor of approximately 2 than in the second. In his examination of these problems from the standpoint of valence theory and the LCAO-MO method, Mulliken concluded that, apart from the repulsion of atoms not linked by valence bonds, account must be taken also of $p-d$ hybridisation, which gives rise to additional stabilisation of the pyramidal phosphine molecule compared with ammonia. Analogous reasoning is applied also to Group VI elements.

Table 1.

Molecule	Valence angle, deg	References	Molecule	Valence angle, deg	References
NH_3	107.3	46	H_2O	104.5	50
PH_3	93.8	47	H_2S	92.1	51
AsH_3	91.8	48	H_2Se	91.0	52
SbH_3	91.3	49	H_2Tl	89.5	53

Recently Hutchinson[55] examined this problem from the standpoint of the strength of hybrid bonds or more precisely the values of the overlap integrals for the s and p orbitals. It was found that the increase of the amount of s character in the hybrid orbitals of elements of the Second Period and the correspondingly greater deviation from a valence angle of 90° leads to an increase of bond strength, since the overlap integral for 2s orbitals is greater than for 2p orbitals. This is not observed in the Third Period and therefore the deviations from an angle of 90° are in this case minimal.

Thus both valence theory and the LCAO-MO method yield merely a qualitative treatment and do not provide an answer to the question why the valence angles in compounds of the elements of the Second Period are close to the tetrahedral value, while in the remaining compounds they are approximately 90°. This was probably the reason for the development of an alternative theory of directed valences—the theory of the repulsion of electron pairs in the valence shell (see for example Refs. 56 and 57 and the literature quoted therein). According to this theory, the formation of directed bonds is due to the repulsion, in consequence of the operation of the Pauli principle, of the electron pairs of the valence shell and the latter can be both unshared and involved in bond formation. In the case of four equivalent pairs, their repulsion leads to the formation of a tetrahedral configuration. The repulsion between lone pairs is more pronounced (the pair occupies a larger proportion of the valence shell) than between bonding pairs, since the latter are located in the field of two nuclei. Accordingly the valence angles of molecules with lone electron pairs are somewhat smaller than the tetrahedral value and this increases on passing from one to two lone pairs (ammonia and water; see Table 1).

In contrast to the elements of the Second Period, the valence shells of which have only four electron pairs, the elements of the Third Period are capable of expanding the valence shell to six electron pairs. Theoretically the number of electron pairs can reach nine but compounds with such coordination have not so far been found. The most likely distribution of these electron pairs is along the angles of a regular octahedron. The bonds formed by these pairs will be at right angles to one another. Probably the 90° angle is limiting and its further decrease involves considerable repulsive forces. The decrease of the limiting valence angle from 109°28′ to 90° on passing from elements in the Second Period to those in higher Periods can be accounted for by the increase of the radius and the decrease of the electronegativity of the central atom, which leads to the removal of the lone pairs to a greater distance from the nucleus and a decrease of the repulsion between them. Thus the repulsion between the lone and shared pairs in elements of the Third and higher Periods leads to a greater mutual approach of the bonds, up to the limiting angle of 90°.

With the aid of this purely qualitative concept and certain auxiliary postulates, it is possible to account for the geometry of a large number of compounds. We may note that recently Bader and Preston[58] criticised these hypotheses.

Whatever the reasons for the differences between the valence angles in elements of the Second Period and higher Periods, the fact of this difference is itself important, since it indicates a difference between the valence states of the elements in these Periods within the limits of a single subgroup, or, in other words, a difference in the nature of the hybridisation of their atomic orbitals.

In order to determine the type of hybridisation, it is possible to employ data for the geometry of molecules and also certain physical methods (nuclear magnetic resonance and nuclear quadrupole resonance).

According to the theory of directed valences, valence angles are determined by the nature of the hybridisation of atomic orbitals. Thus, knowing the valence angles, it is possible to determine the type of hybridisation of the relevant atom in different compounds. However, the use of this principle requires certain assumptions. In the first place it is necessary to assume that the interorbital and internuclear angles are the same, i.e. the bonds are not "bent". For elements the valence shells of which contain only s and p electrons, for example nitrogen, this assumption is quite sufficient to determine the nature of hybridisation, since there is an unambiguous relation between the interorbital angle and the type of $s-p$ hybridisation. The problem of the valence state of elements in higher Periods, in particular phosphorus, is much more complex. The third quantum level contains, apart from the s and p orbitals, also d orbitals, which may be involved in hybridisation. Therefore, in the presence of several types of branching, it is necessary to select orbitals responsible for hybridisation, which always involves certain assumptions. Otherwise several different valence states will correspond to a single valence angle. For example, in phosphorus, which has three types of orbitals, the valence angle of 90° may be due to both the p_3 state and sp^3-d^2 hybridisation.

In determining the type of hybridisation of phosphorus(III) orbitals, one usually starts with the hypothesis that σ bonds are formed by s-p hybrid orbitals. The role of d orbitals in the formation of phosphorus(III) σ bonds is regarded as insignificant and is neglected. However, d orbitals can participate in the formation of π bonds (partial

double bond character). This hybridisation scheme was adopted in a number of studies for the theoretical interpretation of the NMR chemical shifts[59-62], in a discussion of dipole moments and quadrupole interaction constants for halides of Group V elements[63], in quantum-chemical calculations for phosphorus(III) and phosphorus(V) compounds[64-66], and in a number of other investigations[42].

However, we must point out that certain authors considered it necessary to invoke *d* orbitals in order to account for the geometry of the hydrides of Group V elements. Thus in calculations on phosphine Boyd and Lipscomb[67] thought it necessary to take into account the *d* orbitals, since best agreement with experimental data is then obtained. Mulliken used *d* orbitals in a discussion of the valence angles in phosphine[54]. Gordy and coworkers[48-50] considered the valence angles in the hydrides of arsenic, antimony, and sulphur and pointed out the inconsistency between the types of hybridisation determined from the valence angles and from the quadrupole interaction constants; they believe that the reason for this is the absence of an unambiguous correlation between the valence angles and the degree of *sp* hybridisation for elements where *d* orbitals can participate in hybridisation. We may note that the lack of agreement between the results obtained with the aid of the two different approximate methods cannot alone be regarded as proof of the participation of *d* orbitals in hybridisation, but it does demonstrate yet again the approximate nature of the method used to determine the type of hybridisation from the valence angles.

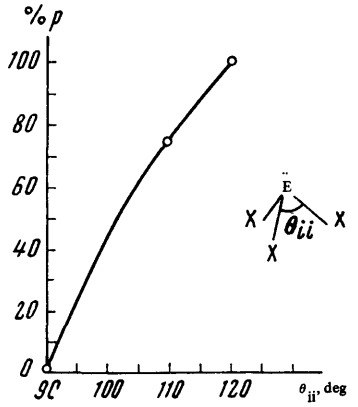


Figure 4. Variation of the percentage *p* character of the orbital of the lone electron pair with the valence angle θ_{ii} for symmetrical EX_3 molecules.

In order to assess the type of hybridisation of the orbitals of the lone electron pair of phosphorus or another element in the molecule of the type EX_3, one may employ a plot relating the amount of *p* character of this orbital to the X–E–X valence angle θ_{ii} (Fig. 4). We constructed such a plot[11] on the basis of three reference points corresponding to the *s*, sp^3, and *p* states of the lone pair. In the *s* state the X–E–X angle formed by the pure *p* orbitals is 90°. When the angle θ_{ii} increases, the amount of *p* character of the lone electron pair will increase and will reach 75% for the tetrahedral configuration (sp^3 hybridisation, 109°28 angle). Therefore an X–E–X angle of 120° (sp^2 hybridisation) will correspond to the full *p* character of the lone electron pair. An analytical expression for this relation was found[12] from the condition for the orthogonality of the hybrid atomic orbitals:

$$\% p = \frac{3\cos\theta_{ii}}{\cos\theta_{ii} - 1} \cdot 100\ \% . \qquad (1)$$

As already stated above, the valence angle in phosphine is approximately 94°C. When methyl groups are combined with the phosphorus atom, the valence angles increase and reach 99° for trimethylphosphine (Table 2).

Table 2. Valence angles in compounds of the type R_nPH_{3-n} ($n = 0-3$).

Compound	Angles			References
	H–P–H	H–P–C	C–P–C	
PH_3	93.8°	—	—	47
CH_3PH_2	93°23′	97°30′	—	68
$(CH_3)_2PH$	—	96°57′	99°.43′	69
$(CH_3)_3P$	—	—	99.1°	70
$(C_6H_5)_3P$	—	—	103.0°*	71
$(C_6H_5)_2PC_6H_4Br$-*p*	—	—	103°*	72
$(C_6H_5C\equiv C)_3P$	—	—	100.7°*	73

*The average valence angle is quoted for the crystal.

In general a valence angle of about 100° is characteristic of the majority of phosphorus(III) compounds and the angle does not usually depend significantly on the type of substituents†. Compounds with methyl, aryl, alkoxy-, dialkylamino-,[77] or halogeno-groups have this angle (Table 3). The valence angles of cyclic compounds (cyclopolyphosphines, phosphorous anhydride) are also close to 100° or somewhat lower[86].

Table 3. Valence angles in compounds of the type PX_3.

X	X-P-X angle, deg	References	X	X-P-X angle, deg	References
F	100.104	78.79	CN	93.5	83
Cl	100	80	C_2H_5O	96.5	84
Br	101.5	81	H_3Si	96.45	85
I	102	82			

Gillespie[56] explained the slight increase of valence angles in phosphorus trihalides on passing from chlorine to iodine (Table 3) by the decrease of electronegativity and the increase of the atomic radius of the halogen. The anomalous (from the standpoint of this relation) angle in phosphorus trifluoride (104°) was regarded as due to a certain amount of double bond character of the P–F bonds, which arises owing to the partial transfer of the lone pair of fluorine to the vacant orbitals of phosphorus or, in

† The 120° valence angle, postulated in trisilylphosphine on the basis of spectroscopic data[74], was not confirmed by an electron diffraction study (Table 3). The valence angle of the phosphorus atom in tri-(*o*-tolyl)-phosphine (117°), calculated by Schindebauer from the dipole moment of this compound[75], is probably incorrect[76].

other words, owing to $p_\pi - d_\pi$ bonding. The increase of electron density in the bonds leads to an increase of the repulsion forces and an increase of the valence angles. Since the mesomeric effect is more pronounced for fluorine than for chlorine, the valence angles in phosphorus trifluoride are greater than in phosphorus trichloride. The hypothesis of $p_\pi - d_\pi$ bonding can probably be used to account for the valence angle of about 100° in the majority of phosphorus(III) compounds, since all the substituents enumerated above, which give rise to this type of angle, are capable of $p_\pi - d_\pi$ interaction (for the methyl group, hyperconjugation is possible). From this point of view, it is interesting that the valence angles in the nitrile group, which is incapable of such conjugation, do not differ from those in phosphine. This applies also to the silyl group, despite its considerable bulk‡.

If this hypothesis is correct, Eqn. (1) will yield a high value for the amount of p character of the lone electron pair, since it was derived on the assumption that the valence angles deviate from 90° only due to s-p hybridisation and no account is taken of the possible additional $p_\pi - d_\pi$ bonding factor and its effect on the geometry of the molecule.

Table 4. The nature of the hybridisation of the lone electron pair of phosphorus in phosphines according to ^{1}H NMR data.

Compound	J_{P-H}, Hz	References	s_p, %	p-character of lone electron pair, %
PH_3	182.2 *	89	6.2	19
CH_3PH_2	+ 187.83 ± 0.03	88	6.4	26
$(CH_3)_2PH$	+ 191.03 ± 0.03	88	6.5	34
$(CH_3)_3P$	—		13.7	41
$C_6H_5PH_2$	201 ± 4 *	90	6.8	32
$(C_6H_5)_2PH$	239 ± 4 *	90	8.2	45
$(C_6H_5)_3P$	—		18.4	55

*J_{P-H} was assumed to be the same as in methylphosphines.

The use of Eqn. (1) leads to the conclusion that, for the majority of phosphorus(III) compounds, the amount of p character of the lone electron pair is 40–50%, which corresponds to an angle of 100° ± 1°. In unsubstituted phosphine, primary phosphines, and trisilyl- and tricyanophosphines, the lone electron pairs have predominantly s character.

For primary and secondary phosphines, the spin–spin splitting constants J_{P-H}, which depend on the amount of s character (s_p, %) of the phosphorus orbital in the P–H bond, can also be used to estimate the nature of the hybridisation of the lone electron pair[88]:

$$J_{P-H} = 29.30\, s_p \qquad (2)$$

This method, based on the same assumptions as the one described above, permits an approximate assessment of the nature of hybridisation in those cases where there are no data for the geometry of the molecule. If it is assumed that the amount of s character of the phosphorus orbital in the P–C bonds of primary and secondary phosphines is the same as in tertiary phosphines (i.e. is clearly too high), then it is possible to calculate by Eqns. (1) and (2) the percentage of s character in the bonding phosphorus orbitals and in the orbital of the lone electron pair. Table 4 lists the values of J_{P-H} for primary and secondary phosphines, the contribution of s_p hybridisation, and the percentage of p character of the lone electron pairs in these compounds; however, these data must of course be regarded as only approximate.

It has been stated that in many cases the ^{31}P NMR chemical shifts for phosphorus(III) compounds can be used for the same purposes[60].

The valence angles in nitrogen(III) compounds are usually larger than in the corresponding phosphines and in ammonia and alkylamines are close to the tetrahedral value (Table 5). The introduction at the nitrogen atom of substituents capable of $p-\pi$ conjugation [phenyl and carbonyl groups and a phosphorus(III) or phosphoryl group[77]] increases the valence angles approximately by 10° to a value approaching 120°. Correspondingly, the lone electron pair of nitrogen is of the p type to the extent of 70% and above. In those cases where the valence angle is close to 120° the lone electron pair is almost entirely of the p type.

Thus the assessment of the type of hybridisation from valence angles or by other methods leads to the conclusion that the lone electron pair of phosphorus(III) differs from that in nitrogen in analogous compounds by having a much smaller amount of p character. An increase of the amount of p character is also observed on passing from phosphorus to sulphur.

Table 5. Valence angles in compounds of the type R_nNH_{3-n} (n = 0–3).

Compound	Angles			References
	H–N–H, deg	H–N–C, deg	C–N–C, deg	
NH_3	107.3	—	—	46
CH_3NH_2	105.8	112.2	—	91
$(CH_3)_2NH$	—	108.8	112.2	92
$(CH_3)_3N$	—	—	110.6	93
$(C_6H_5)_3N$	—	—	116	94
$HCONH_2$	118.53	120.37	—	95
$C_6H_5N(CH_3)_2$	—	—	116 *	96
$(SiH_3)_3N$	—	—	119.6 **	97
$(CH_3)_2NPCl_2$	—	—	120 *	77
$(CH_3)_2NP(O)Cl_2$	—	—	116 *	77

*Average angle at the N atom.
**Si–N–Si angle.

In contrast to phosphorus, sulphur has a second lone electron pair. With a valence angle of 90°, σ bonds should be formed by pure p orbitals. Then, if one of the lone pairs is fully of the s type, the other is a purely p electron pair. In the hybridisation of the orbitals of the lone electron pairs the amount of p character will vary from 100 to 50% (sp hybridisation). When the hydrogen atoms in hydrogen sulphide are replaced by alkyl or aryl

‡ We may note that the valence angles of the tricyanomethane anion[87], an electronic analogue of tricyanophosphine, amount to about 119.5° in $NH_4C(CN)_3$.

groups, the valence angles are found to increase (Table 6) with a corresponding increase of the amount of p character of the lone electron pairs, which reaches about 72% in the case of diphenyl sulphide§.

Chlorine has three lone electron pairs of which one may be of the s type and the other two of the p type in the limiting case. For sp^2 hybridisation, the amount of p character of any of the lone electron pairs will be 66.6%.

Table 6. Angles in compounds of the type R_nSH_{2-n} ($n = 0-2$).

Compound	Angles			References
	H—S—H, deg	H—S—C, deg	C—S—C, deg	
H_2S	92.1	—	—	51
CH_3SH	—	96°30′	—	98
$(CH_3)_2S$	—	—	98°54′	99
$(C_6H_5)_2S$	—	—	113°	100,101

Thus a distinctive feature of the structure of the valence shell of phosphorus(III) is a reduced amount of p character of the lone electron pair compared with the other elements of Periods II and III. This feature is reflected in the physical and chemical properties and in the capacity of the lone electron pair for $p-\pi$ conjugation.

III. $p-\pi$ CONJUGATION AND THE HYBRIDISATION OF THE LONE PAIR OF ELECTRONS

As already stated in the introduction, the capacity of the lone electron pair of any element for $p-\pi$ conjugation depends on the position of this element in the Periodic System and hence on the quantum level where the lone pair is located and, within the limits of a single Period, on the nuclear charge or the electronegativity of the element.

Yet another factor, which is usually hardly taken into account, namely the nature of the hybridisation of the electron pair¶, should play an important role[12]. Indeed, p or d orbitals are necessary for the formation of π bonds; s orbitals are incapable of interaction with p_Z orbitals, since the overlap integral S_{AB} of the s orbital of the A atom with the p_Z orbital of the B atom is zero[45], as shown in Fig. 5 taken from Coulson's book[45]. It follows from Fig. 5 that, by virtue of the difference in sign between the two parts of the p function, the integrand in $S_{AB} = \int \Psi_A \Psi_B \, d\tau$ is the sum of two terms equal in magnitude but opposite in sign (the elements $d\tau_1$ and $d\tau_2$ located symmetrically relative to AB axis correspond to these terms)[45]. The overlap integral becomes zero by virtue of symmetry properties. Thus p and sp hybrid lone electron pairs are capable of $p-\pi$ conjugation and in the latter case the capacity for conjugation is determined by the amount of p character of the lone pair.

§ The amount of p character of the orbital forming the σ bond was calculated from the formula

$$p = \frac{1}{1-\cos\theta_{ii}} \cdot 100\,\%,$$

where θ_{ii} is the valence angle.

¶ This problem was dealt with very briefly by Higashi et al.[102]

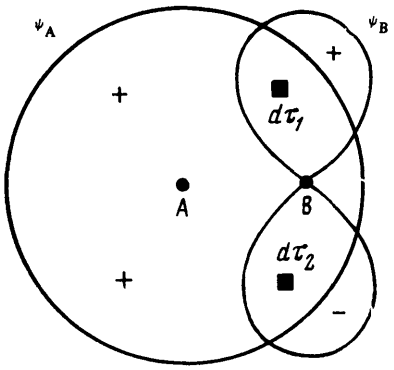


Figure 5. Schematic illustration[45] of the equality to zero of the S_{AB} overlap integral of the s orbital (Ψ_A) with the p_Z orbital (Ψ_B).

As shown above, the lone electron pair of phosphorus has a reduced amount of p character compared with the lone pairs of nitrogen, sulphur, and other elements in Periods II and III. Thus one may expect that in the case of phosphorus(III) $p-\pi$ conjugation in the ground state will be either greatly weakened and masked by other effects or, when the percentage of p character is very small, will be absent altogether. The experimental confirmation of this conclusion will be discussed below.

IV. PROPERTIES OF PHOSPHORUS(III) COMPOUNDS IN THE OPTICALLY UNEXCITED STATE

A. PHYSICAL PROPERTIES

1. Configuration Stability of Phosphorus(III) Compounds

A remarkable property of phosphorus(III) compounds is their configurational stability, which leads to optical activity in asymmetric molecules. This characteristic, which very sharply distinguishes phosphorus(III) compounds from the corresponding nitrogen(III) derivatives, is caused by the high energy barrier to the inversion of the pyramidal configuration of phosphorus associated with the high deformation energy of its valence angles. Theoretical calculations of the energy barrier to inversion yielded different results†. Here we shall note only the most correct calculations by Weston[108], which indicate that optically active phosphines may exist. Weston showed that phosphines have much higher energy barriers to inversion than amines (Table 7) and calculated the rate constants for their racemisation. For trimethylphosphine, the period of 50% racemisation at 20°C proved to be about 1 h. Hence Weston concluded that the optical isomerism of phosphines can be observed only at low temperature. Horner and Winkler[107] showed experimentally that optically active phosphines are more stable (in the sense of the retention of their configuration) than follows from Weston's calculations. They not only retain their optical activity at room temperature but can also be distilled without appreciable racemisation. Measurements of the rate of racemisation

† A good description of the history of this problem is given in McEwen's review[103]; see also other reviews[104,105].

at 130°C gave a high activation energy for the racemisation of dextrorotatory methylphenylpropylphosphine (about 30 kcal mole^{-1}). For the less stable diphosphines[108], where a rapid change in configuration occurs above 125°C, the activation energy for inversion is 26 ± 2 kcal mole^{-1} according to NMR data. It is interesting that changes in configuration are also not observed in many reactions involving the lone electron pair[103]. Configurational stability is characteristic not only of phosphines but also of the esters of phosphorus(III) acids, as shown by the geometrical isomerism of a number of five- and six-membered cyclic phosphites observed by the NMR method[109-119].

Table 7. Barriers to inversion of compounds of Group V elements according to spectroscopic data[106].

Compound	Inversion barrier, kcal mole^{-1}	Compound	Inversion barrier, kcal mole^{-1}	Compound	Inversion barrier, kcal mole^{-1}
NH_3	5.93	$P(CH_3)_3$	22.0	AsH_3	35.0
$N(CH_3)_3$	8.19	PF_3	45.1	$As(CH_3)_3$	29.2
PH_3	31.8	PCl_3	68.1	$Sb(CH_3)_3$	26.7

Thus phosphorus differs from nitrogen not only by the smaller valence angles but also by the stability of the pyramidal configuration, the change in valence angles requiring a significant expenditure of energy. The stability of the configuration has a most direct bearing on the problem of $p-\pi$ conjugation. The point is that, for $p-\pi$ conjugation to be appreciable, a significant increase of the amount of p character of the lone pair and a corresponding increase in valence angles is necessary. Then the energy expenditure on the deformation of valence angles cannot be compensated by the conjugation energy, since even in the most favourable case (conjugation of the amino-group with the benzene ring) the resonance energy does not exceed[117] about 10 kcal mole^{-1} and for the phosphino-group it can be considerably less. Hence it becomes understandable why valence angles at the phosphorus atoms do not increase even in the presence of substituents capable of conjugation with the lone electron pair.

Probably the above relation between the optical activity of phosphines and the low tendency of the lone electron pair of phosphorus towards $p-\pi$ conjugation is more general and is not characteristic solely of phosphorus. One may suppose that the absence of $p-\pi$ conjugation (or only insignificant conjugation) can be expected for those classes of compounds, asymmetric representatives of which can exist in an optically active form despite the presence of lone electron pair at the asymmetric central atom. This criterion may be employed in the discussion of the problems of $p-\pi$ conjugation in those cases where the molecular geometry is unknown.

2. Dipole Moments of Phosphines

In a discussion of the dipole moments of phosphines in connection with the problems of $p-\pi$ conjugation, three problems are of primary interest: the effect on the dipole moments of the nature of hybridisation of the phosphorus orbitals; the direction of the dipole moment in aliphatic and aromatic phosphines; the magnitude and direction of the mesomeric dipole moment.

Table 8 lists the dipole moments of unsubstituted phosphine, primary, secondary, and tertiary phosphines, and also ammonia and the corresponding amines. The lower dipole moment of unsubstituted phosphine compared with ammonia shows in particular that, in contrast to the lone pair of nitrogen, that of phosphorus makes an insignificant contribution to the overall dipole moment of the molecule. This is probably evidence of a greater amount of s character of the lone electron pair of phosphorus compared with nitrogen[125]. When the hydrogen atoms in phosphine are replaced by alkyl groups, a gradual increase of the dipole moment is observed, which is probably due, on the one hand, to the positive inductive effect of the alkyl groups and, on the other hand, to the increase of the moment of the lone pair due to the increase in the amount of its p character. It is interesting to note that the opposite tendency obtains for amines; on passing from ammonia to tertiary amines, the dipole moment falls (Table 8). Possibly this is caused by a lowering of the moment of the lone electron pair[125] as a result of the increase in the amount of its p character. The point is that the purely s and p electron pairs do not have a dipole moment by virtue of the symmetry of their orbitals[102]. Hybridisation leads to the appearance of a dipole moment, which is a maximum in the case of the sp state. An increase in the amount of p character of the lone electron pair from 50 to 100% or its decrease from 50 to 0% will reduce the dipole moment. These opposed tendencies in the variation of the dipole moments of amines and phosphines yet again demonstrate the different natures of their lone electron pairs.

Table 8. Dipole moments of aliphatic phosphines and amines.

Type of compound	Dipole moment			
	X=P	References	X = N	References
XH_3	0.579±0.012, gas	118	1.47, gas	119
CH_3XH_2	1.100±0.010, gas	68	1.283, gas	120
$C_2H_5XH_2$	1.17 ±0.02, gas	121	1.225, gas	122
	1.11 ±0.05, benzene	121		
$(CH_3)_2XH$	1.23 ±0.01, gas	69	1.02, gas	123
$(C_2H_5)_2XH$	1.39 ±0.06, benzene	121	0.920, gas	122
$(CH_3)_3X$	1.192±0.005, gas	70	0.612±0.003, gas	93,124
$(C_2H_5)_3X$	1.45 ±0.05, benzene	121	0.660, gas	122

The direction of the dipole moments in aromatic phosphines was determined by Sutton and coworkers[126], Klages and Langpape[127]‡, and also Schindlbauer and Hajek[129]. The direction of the moments in aliphatic amines and phosphines is the same, the negative pole of the dipole being located at the heteroatom. In aromatic amines the sign of the dipole moment changes as a result of $p-\pi$ conjugation and the benzene ring becomes the negative pole. On the other hand, in aromatic phosphines the direction of the dipole moment is maintained: the negative pole is the phosphorus atom as before. This follows from a comparison of the dipole moments of *para*-substituted phosphines: electron-donating substituents in the *para*-position increase and electronegative substituents decrease the moment (Table 9). A similar phenomenon is observed

‡ Klages and Langpape[127] quote unduly high dipole moments of trialkylphosphines, which were not confirmed by subsequent studies[121,128].

also in halogenobenzenes. Here too the direction of the dipole moment also remains unchanged, but its magnitude is reduced, mainly owing to $p-\pi$ conjugation[1]. In this case the mesomeric moment can be readily estimated approximately by Sutton's rule[1,130,131], namely from the difference between the dipole moments of aromatic and aliphatic compounds. This rule is known to apply only to regular groups, the direction of the dipole moments of which coincides with the direction of the benzene ring–substituent bond. In other cases vector subtraction is necessary. The mesomeric moment of dialkylphosphino-groups has not yet been determined. However, simple comparison of the dipole moments of aromatic and aliphatic compounds can lead to certain interesting conclusions. Thus, on passing from trimethylphosphine to dimethylphenylphosphine, a slight increase of the dipole moment is observed (Table 10). When a correction is applied for the effect of the solvent[121], the difference is somewhat reduced.

Table 9. Effect of *para*-substitution on the dipole moments of aromatic phosphines and amines.

Type of compound	Dipole moments			
	X = P	References	X = N	References
$C_6H_5XH_2$	1.11, hexane	129	1.54, hexane	129
p-$CH_3C_6H_4XH_2$	1.41, hexane	129	1.35, hexane	129
$C_6H_5X(C_4H_9)_2$	1.45, hexane	129	1.91, hexane	129
p-$CH_3C_6H_4X(C_4H_9)_2$	1.55, hexane	129	1.57, hexane	129
$(C_6H_5)_3X$	1.49, benzene	128		
$(p$-$CH_3C_6H_4)_3X$	1.92, cyclohexane	127		
$(p$-$Cl(C_6H_4)_3X$	0.65, benzene	126		

The decrease of the dipole moment may be due to the inductive effect of the phenyl group and the effect of $p-\pi$ conjugation (when it occurs). The moment may increase owing to $p_\pi-d_\pi$ conjugation or as a result of an increase in the moment of the lone electron pair (an increase in the valence angle). One may assume that the valence angles do not change significantly when the methyl group is replaced by a phenyl group. Since there is no decrease of the dipole moment on passing from trimethylphosphine to dimethylphenylphosphine, one must conclude that $p-\pi$ conjugation does not play an appreciable role and the mesomeric effect is due to $p_\pi-d_\pi$ conjugation. This conclusion is confirmed by a comparison of the moments of other aliphatic and aromatic phosphines (Table 9)§.

The weak π-donor capacity of phosphorus is indicated also by the dipole moments of phosphinoboranes R_2BPR_2 determined by Coates and Livingstone[132]. The lone electron pair of phosphorus interacts to a very slight degree (if at all) with the vacant p orbital of boron. Here phosphorus also constitutes the negative pole of the dipole. As a result of the conjugation of the lone electron pair of nitrogen with the p orbital of boron, in dialkylamino-boranes the negative pole is displaced to boron. Coates and Livingstone find this behaviour of phosphorus surprising and account for it by the different dimensions of the $2p$ orbital of boron and the $3p$ orbital of phosphorus. Without denying the role of this factor, we may, however, point out that the principal cause of this behaviour should probably be sought in the different nature of the hybridisation of the lone electron pairs of phosphorus and nitrogen.

Table 10. Comparison of the dipole moments of aliphatic and aromatic phosphines.

Compound	Dipole moment	References	Dipole moment	References
CH_3PH_2	1.100, gas	68	—	—
$C_6H_5PH_2$	1.11, hexane	129	—	—
$(CH_3)_3P$	1.192, gas	70		—
$C_6H_5P(CH_3)_2$	1.31, hexane	129	1.22, cyclohexane	127
$(C_2H_5)_3P$	1.45, benzene	121	1.48, benzene	128
$C_6H_5P(C_2H_5)_2$	1.45, benzene	129	1.40, dioxan	133
$(C_6H_5)_2PC_2H_5$	1.46, dioxan	133	1.35, cyclohexane	127
$(C_6H_5)_3P$	1.49, benzene	128	1.44, cyclohexane	127
$(C_4H_9)_3P$	1.49, benzene	128		
$C_6H_5P(C_4H_9)_2$	1.45, hexane	129		

The problem arises whether systems with phosphorus-(III) are possible in which $p-\pi$ conjugation in the ground state plays an appreciable role and whether there are methods whereby it can be observed. A sufficiently clear-cut answer cannot at present be given. If the above method of estimation of the nature of the hybridisation of orbitals from the valence angles yields the correct information about the valence state of phosphorus despite the assumptions made, one may postulate that such cases should occur. According to an estimate, the lone electron pair in tertiary amines has approximately 50% of p character. If such a pair is conjugated with a powerful electron-accepting substituent, the energy of $p-\pi$ interaction can also be appreciable. One cannot exclude the possibility that such conjugation would be reflected in the chemical or physical properties of the compound.

Goetz and coworkers[133,134] measured the dipole moments of substituted arylphosphines of the type p-$XC_6H_4P(C_6H_5)_2$ and p-$XC_6H_4P(C_2H_5)_2$. It was found that the observed dipole moments are usually higher than the values calculated assuming additivity. In the case of electron-donating substituents (methoxy- and dimethylamino-groups) this is evidence of $p_\pi-d_\pi$ conjugation, since $p-\pi$ conjugation may be postulated for halogens. It is remarkable that the differences between the observed and calculated dipole moments of diphenyl-p-methoxyphenyl- and p-dimethylaminophenyl-phosphines proved to be significantly greater than for their oxides and sulphides: the $p_\pi-d_\pi$ conjugation in the oxides and sulphides must be considerably more pronounced than in the phosphines. We may note that the observed and calculated dipole moments of tri-(p-chlorophenyl)-phosphine are identical. According to the data of other workers[136], the dipole moment of cyanodiphenylphosphine also agrees with the value calculated assuming additivity. Possibly the above differences between the observed and calculated dipole moments are not associated with $p-\pi$ conjugation but with other factors, in particular the imperfection of the model chosen for the calculations.

§ Using the high dipole moments of trialkylphosphines quoted by Klages and Langpape[127], Hudson[41] concluded that the lowering of the dipole moment on passing to aromatic phosphines is due to $p-\pi$ conjugation. This conclusion is open to objection, since the data of Klages and Langpape were not confirmed.

Thus one cannot at present give a definite answer to the question of the possible $p-\pi$ conjugation in systems with electron-accepting substituents posed above.

B. CHEMICAL AND PHYSICOCHEMICAL PROPERTIES

The study of the directive influence in electrophilic substitution in the benzene ring constitutes a classical chemical procedure for the investigation of the electronic effect of the substituent. Unfortunately this method cannot be applied to phosphorus(III) compounds because of the high nucleophilicity of phosphorus(III) itself, which leads to preferential attack of the electrophilic agent on the phosphorus atom. Nucleophilic substitution in aromatic phosphorus compounds is so far unknown. The only example of a direct investigation of the directive influence of phosphorus(III) is that of the nucleophilic addition of vinyl derivatives of phosphorus(III) to a double bond. It was in fact first employed for this purpose.

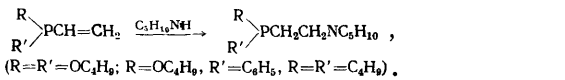
The electronic effect of groups with phosphorus(III) is investigated mainly by physicochemical methods, whereby it is possible to elucidate the nature of the resonance effects by indirect procedures. At the present time there exist two different approaches. The first of these is associated with the study of the effect of phosphorus(III) on the properties of the functional groups in the same benzene ring. The use of correlation analysis methods, in particular the Hammett equation, permits an indirect determination of the nature of the directive effect of the substituent. Valuable information about the nature of the π-electronic effects of phosphorus(III) is provided by protophilic deuterium exchange in aromatic phosphines and a number of other chemical properties. The second approach is based on reactions in which phosphorus is the reaction centre. This involves the study of the effect of substituents at the phosphorus atom on the reactivity of the lone electron pair, which permits an assessment of its capacity for delocalisation (the basicity of phosphines, alkylation reactions, and the addition of sulphur).

1. Electronic Effects of Phosphorus(III) as a Substituent

a. Directive influence in the addition of piperidine to vinyl derivatives of phosphorus(III). According to their directive influence in reactions involving ionic addition to vinyl derivatives of the type $CH_2=CH-X$, the substituents X can be divided into two types: the first includes π-donor groups, which as a rule direct the ionic part of the reactant to the α-position in relation to the substituent and the second group includes electron-accepting groups directing the reactant to the β-position. Substances of the first type, for example alkyl vinyl ethers and vinylamines, show a greater tendency to combine with electrophilic agents; substances of the second type, for example acrylonitrile, combine more readily with nucleophilic agents.

Vinyl derivatives of phosphorus(V) are typical electrophilic systems and readily combine with nucleophilic agents. It has been shown[6-8,137,138] that in all cases of addition the reactant is directed to the β-position regardless of the nature of the group at the phosphorus atom.

It was found unexpectedly[6-8] that the same type of directive influence is characteristic also of the vinyl compounds of phosphorus(III), although their reactivity is much lower than that of the phosphorus(V) compounds. The addition of piperidine was observed only under the conditions of prolonged heating of the reactants at 140–160°C:



$(R=R'=OC_4H_9;\ R=OC_4H_9,\ R'=C_6H_5,\ R=R'=C_4H_9)$.

The most reactive are the esters of vinylphosphonous and phenylvinylphosphinous acids, which combine with piperidine in the absence of catalysts. Piperidine hydrochloride accelerates the reaction but does not alter the site at which the addition takes place. The replacement of both butoxy-groups by phenyl groups leads to a sharp decrease of the reactivity of the double bond: in the absence of a catalyst and even in the presence of an acid catalyst, the addition could not be achieved. In the case of the more electropositive dibutylphosphino-group, the addition under the influence of piperidine hydrochloride still takes place, possibly owing to the formation of dibutylvinylphosphine hydrochloride.

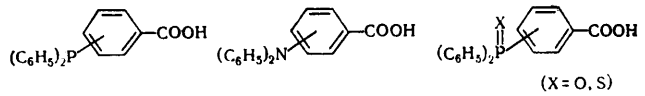
Thus, as regards the directive influence in the addition reaction, phosphorus(III) resembles silicon, which does not have a lone electron pair and for which a β-directing effect is also typical[139,140]. Later a β-directing effect was observed in the reaction of lithium diphenylphosphide with β-diphenylphosphinostyrene[141] and also in the reaction of butyl-lithium with vinylphosphines[142]. We may note that β-addition under the influence of a powerful nucleophilic agent such as butyl-lithium was also observed with phenyl vinyl sulphide[143]. Recently a β-directing effect was observed[144] in the addition of diphenylphosphine and diphenylarsine to vinyl- and ethynyl-phosphines in the presence of basic catalysts. The reaction of vinyl phosphorus(III) compounds with phenyliminobenzonitrile can be regarded as evidence in favour of a β-directing effect of substituents with phosphorus(III).[145,146]

The β-directing effect in the non-catalytic addition of piperidine is evidence either of the absence or of the insignificance of the π-donor effect in phosphorus(III). Its electron-accepting influence on the polarisation of the multiple bond or its stabilising effect on the transition state can be accounted for by $p\pi-d\pi$ conjugation and possibly by an inductive effect (since the electronegativities of H and P are the same and the inductive effect of the group will depend on the substituents at the phosphorus atom).

The data for the frequencies of the C=C stretching vibrations in the Raman spectra of vinyl and allyl derivatives of phosphorus(III) also agree with the conclusion that $p-\pi$ conjugation is absent[147]. A characteristic feature of $p-\pi$ conjugation—an increase in the integrated intensity of the double bond line, which is fairly distinct for the vinyl derivatives of nitrogen and sulphur and is not observed in vinylsilanes—is absent from the spectra. Vinyl derivatives of phosphorus(III) differ little from alk-1-enes as regards the spectroscopic effect of the double bond. Thus, according to both chemical and spectroscopic characteristics, vinyl compounds of phosphorus(III) are closer to vinylsilanes than to vinyl sulphides and vinylamines.

b. Effect of substituents with phosphorus(III) on the properties of functional groups in the benzene ring. For the investigation of the directive influence of phosphorus(III), indirect methods, in particular correlation analysis, have also been successfully employed. The authors of the present

review together with Lobanov[9,10,148] determined the ionisation constants of *m*- and *p*-diphenylphosphinobenzoic acids and for comparison the ionisation constants of *m*- and *p*-diphenylaminobenzoic acids and the corresponding benzoic acids containing groups with phosphorus(V):



The results are presented in Table 11. It was found that, regardless of the valence of phosphorus, all the phosphorus-containing substituents investigated increase the ionisation constant of benzoic acid and are therefore electron acceptors. Correspondingly Hammett's σ constants for phosphorus-containing substituents are positive.

Table 11. Ionisation constant (pK_a) of phosphorus-substituted benzoic acids XC_6H_4COOH and the σ, σ_I, and σ_R constants of the substituents X [1 : 1 (by volume) aqueous alcohol, 25°C].[9,10,148]

X	pK_a	$\frac{k_{meta}}{k_{para}}$	σ	$\sigma_p-\sigma_m$	σ_I	σ_R
H	5.72	1	0.00	0.00	0.00	0.00
p-$(C_6H_5)_2P$	5.39	0.76	0.19	0.08	0.05	0.14
m-$(C_6H_5)_2P$	5.51		0.11			
p-$(C_6H_5)_2N$	6.10	—	−0.29	—	—	—
m-$(C_6H_5)_2N$	5.77	2.18	−0.07	−0.22	0.11	−0.40
p-$(C_6H_5)_2P(O)$	4.88	—	0.53	—	—	—
m-$(C_6H_5)_2P(O)$	5.11	0.58	0.38	0.15	0.27	0.26
p-$(C_6H_5)_2P(S)$	4.97	—	0.47	—	—	—
m-$(C_6H_5)_2P(S)$	5.24	0.54	0.29	0.18	0.15	0.32

It is significant that *para*-phosphorus-substituted acids are stronger than the *meta*-substituted acids. This is evident from the ratios k_{meta}/k_{para}, which are less than unity, and also from the positive differences $\sigma_p - \sigma_m$, which are characteristic of *meta*-directing groups. Consequently all the phosphorus-containing substituents investigated are *meta*-directing. On the other hand, as was to be expected, the diphenylamino-group lowers the ionisation constant of benzoic acid to a greater extent when present in the *para*-position than when present in the *meta*-position and is thus an ortho-*para*-directing substituent.

The inductive (σ_I) and resonance (σ_R) components of Hammett's constants were calculated[148] from the constants σ_m and σ_p (Table 11). These values particularly clearly illustrate the nature of the electronic effect of substituents with phosphorus(III) and phosphorus(V). The inductive effect of the diphenylphosphino-group proved to be small, in agreement with the electronegativity of phosphorus. The groups with phosphorus(V) are of course characterised by larger inductive constants. The inductive effect of the diphenylamino-group exceeds that of the diphenylphosphino-group, which is consistent with the difference between the electronegativities of nitrogen and phosphorus (3.0 and 2.1 according to Pauling). The resonance effects of phosphorus-containing groups, particularly the diphenylphosphino-group, are interesting. It has been found that, in contrast to the diphenylamino-group, the diphenylphosphino-group is a π-electron acceptor despite the presence of a lone electron pair. The diphenylamino-group is a π-donor substituent, although its mesomeric effect is of course somewhat reduced compared with that of dialkylamino-groups. The resonance effects of substituents with phosphorus(V) are positive and exceed the resonance effect of the diphenylphosphino-group. These results permit an approximate estimation of the $p-\pi$ conjugation effect. The difference in the values of σ_R for the diphenylphosphino- and diphenylphosphinyl groups is caused, on the one hand, by the increase of the extent of $p_\pi - d_\pi$ conjugation owing to the presence of a positive charge at the phosphorus(V) atom and some compression of *d* orbitals and, on the other hand, by the absence of $p-\pi$ conjugation, which may occur in the case of phosphorus(III). We cannot estimate the contribution of each effect but the overall contribution, i.e. the difference between the values of σ_R for these groups, is very insignificant and amounts to only 0.12, which most probably indicates that the effect of $p-\pi$ conjugation is close to zero for the diphenylphosphino-group.

These results were later confirmed by other workers[16-29]. Unfortunately there is no information in the literature for *meta*-substituents with phosphorus(III) exception for the data quoted above. The results of Schiemenz[19,20] for phosphorus-containing groups in the *para*-position virtually agree with those obtained by ourselves. Somewhat different values of σ_p were found by Baldwin et al.[22] from the ionisation constants of phosphorus-substituted benzoic and arylphosphonic acids in aqueous tetrahydrofuran (THF). They are low for all phosphorus-containing groups. This may be associated with the effect of the solvent.

Table 12. Ionisation constants (pK_a) of phosphorus-substituted phenols XC_6H_4OH and the constants σ^-, σ_m, and $\sigma_{\bar{R}}$ of the substituents X [1 : 1 (by volume) aqueous alcohol, 25°C].[13,149-151]

X	pK_a	σ^-	$\overline{\sigma_I}$ (Refs.19 & 20)	σ	$\sigma^- - \sigma_p$	$\sigma_{\bar{R}}$
H	11.21	0.00	0.00	0.00	0.00	0.00
p-$(C_6H_5)_2P$	10.46	0.26	0.32	0.19	0.07	0.16
p-$(C_6H_5)_2P(O)$	9.38	0.68	0.88	0.53	0.15	0.35
p-$(C_6H_5)_2P(S)$	9.49	0.63	0.73	0.47	0.16	0.44
m-$(C_6H_5)_2P$	10.82	—	—	0.12	—	—
m-$(C_6H_5)_2P(O)$	10.05	—	—	0.42	—	—
m-$(C_6H_5)_2P(S)$	10.14	—	—	0.38	—	—
p-$(CH_3)_2P$	10.67	0.18	—	—	—	—
p-$(CH_3)_2P(O)$	9.58	0.60	—	—	—	—
p-$(CH_3)_2P(S)$	9.58	0.60	—	—	—	—
m-$(CH_3)_2P$	10.90	—	—	0.09	—	—
m-$(CH_3)_2P(O)$	10.13	—	—	0.39	—	—
m-$(CH_3)_2P(S)$	10.02	—	—	0.43	—	—

Makhamatkhanov and the authors of the review[13,149-151] measured the pK_a of *meta*- and *para*-phosphorus-substituted phenols. Schiemenz measured the pK_a of *para*-phosphorus-substituted dimethylanilines[19,20]. The nucleophilic constants σ^- calculated from these data, which characterise the effect of electron-accepting substituents in the case of an electron-donating reaction centre, and the constants σ_m are listed in Table 12. These results differ somewhat from those of Schiemenz, probably owing to the difference in the reaction series¶. The σ^- constants for phosphorus-containing substituents are positive and exceed

¶ It is known that the constants σ^- are not universal and depend strongly on the nature of the reaction centre and the type of reaction.

the corresponding Hammett constants σ_p, which is evidence of an effect of the direct polar conjugation of the phosphorus-containing groups with the reaction centre. The difference $\sigma^- - \sigma_p$ for the diphenylphosphino-group is 0.07 in phenols and 0.13 in substituted dimethylanilines. Thus the electron-accepting effect of the direct polar conjugation of phosphorus(III) with the electron-donating reaction centre is small but distinct. The constants σ_m for phosphorus-containing groups, determined from the pK_a of the corresponding phenols and benzoic acids, agree satisfactorily among one another.

The constants σ^- and σ_m for the dimethylphosphino-group were found from the ionisation constants of dimethylphosphinophenols[150,151] (Table 12). They proved to differ little from the analogous constants for the diphenylphosphino-group.

Analogous results were obtained also for other reaction series. Thus positive albeit somewhat high values of σ_p for the diphenylphosphino-group (0.3 and 0.5) were derived from data for the reactivity of *p*-diphenylphosphinostyrene in copolymerisation with styrene and methyl methacrylate[152]. The constant σ_p for the diethylphosphino-group (0.03) was determined by Stepanov et al.[17] from the basicity of tetraethyl-*p*-phenylenediphosphine. The significant difference between this value and σ_p for the dimethylamino-group (−0.83) is noteworthy.

c. Electronic effect of substituents with phosphorus(III) according to data obtained by various physical methods. The electronic effect of phosphorus-containing groups was investigated by physical methods (infrared spectroscopy[18,19] and ^{13}C NMR, ^1H NMR, and ^{19}F NMR spectroscopy[23-32,153,154]) and in many cases the corresponding σ constants were determined. On the whole, these data agree with the results derived by chemical methods. The systematic study of the electronic effect of phosphorus-containing groups with the aid of ^{19}F NMR, undertaken by Taft and coworkers[27,38], Johnson and Jones[29], and also Schindlbauer and Prikoszovich[26,153,154], is of greatest interest. The σ constants which they found in many cases agree well with our data but the resolution into inductive and resonance components is somewhat different: according to ^{19}F NMR data, the σ_I constants are somewhat high and the resonance constants σ_R are low compared with the chemical results. It is noteworthy that the data of the above workers do not always agree with one another (Table 13). This is precisely why much importance cannot be attributed to the negative values of $\bar{\sigma}_R$ for the dimethylphosphino- and bis(dimethylamino)phosphino-groups. According to the results of a study of pentafluorophenyl phosphorus(III) compounds, dimethyl- and diphenyl-phosphino-groups are π-acceptor substituents[30-32] (see also other investigations[33-38]). ^1H NMR and ^{13}C NMR data for dialkylethynylphosphines also indicate a π-electron accepting effect of dialkylphosphino-groups[39,40]. Probably the problem of the exact estimation of the resonance and inductive effects of dialkylphosphino- and related groups with phosphorus(III) cannot be regarded as finally solved†, but it is already clear that the resonance effect of dialkylphosphino-groups is close to zero.

† For example, it is not clear why σ_I for the dimethoxyphosphino-group is smaller than for the dimethylphosphino-group (Table 13), since the opposite relations are observed for substituents with phosphorus(V).[143] The reason for the large value of σ_I for the dimethylphosphino-group compared with the bis(dimethylamino)phosphino-group is also obscure.

The ^1H NMR spectrum of triphenylphosphine indicates a small effect of the diphenylphosphino-group on the magnetic screening of the ring protons compared with benzene[155,156]. The type of spectrum changes from a singlet to a doublet depending on the solvent and the concentration of triphenylphosphine, which is evidence of a similarity of the chemical shifts of *o*-, *m*-, and *p*-protons[155]. On passing from deuterochloroform to hexadeuterobenzene, the spectrum is split and the signal of *o*-protons shifts by 0.09 p.p.m. towards weaker fields and those of *m*- and *p*-protons shift by 0.25 p.p.m. towards stronger fields, but the exact values of the chemical shifts have not yet been determined[156].

Table 13. The constant σ_I and $\sigma_{\bar{R}}$ of phosphorus-containing groups X_2P according to ^{19}F NMR data for phosphorus-containing fluorobenzenes.

X	σ_I		σ_R	
	Refs.27 & 28	Refs.26,153 & 154	Refs.27 & 28	Refs.26,153 & 154
H	—	+0.07	—	+0.17
CH_3	+0.06	+0.06	−0.06	+0.16
CH_3O	+0.16	—	+0.05	—
$(CH_3)_2N$	−0.05	—	−0.05	—
C_6H_5	+0.18	+0.21	0.00	+0.09
F	+0.39	—	+0.16	—
Cl	+0.43	+0.44	+0.16	+0.25
CF_3	+0.52	—	+0.16	—
CN	+0.58	—	+0.19	—

The ESR spectra of the radical-anions obtained from triphenylphosphine[157] and dimethylphenylphosphine[158] show that the diphenyl- and dimethyl-phosphino-groups are electron-accepting substituents according to their influence on the distribution of spin density‡. The ESR spectra of 2,6-di-t-butylphenoxy-radicals containing substituents with phosphorus(III) and phosphorus(V) in the 4-position lead to a similar conclusion[160].

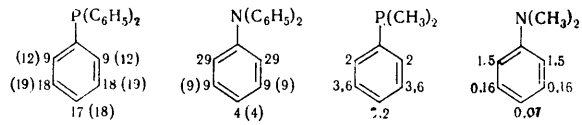
The different capacities of the lone electron pairs of nitrogen and phosphorus for resonance delocalisation are clearly shown in the mass spectra of the compounds of these elements. The principal fragment formed on electron impact from the bis(diphenylamino)methane molecule[161] is the resonance-stabilised cation $(C_6H_5)_2\overset{+}{N}=CH_2$. The analogous diphosphinomethane gives rise to a more complex spectrum of fragments, among which species arising as a result of the migration of the phenyl group predominate: $C_6H_5\overset{+}{P}\equiv CH$ and $(C_6H_5)_3\overset{+}{P}$. The $(C_6H_5)_2\overset{+}{P}=CH_2$ fragment is formed in a smaller amount[161]. Comparison of the mass spectra of other phosphorus and nitrogen compounds lead to the same conclusions[162].

Thus physical methods confirm more or less convincingly the results of chemical studies.

d. Effect of substituents with phosphorus(III) on the rate of protophilic deuterium exchange in arylphosphines. It appears that at the present time one reaction involving the direct substitution of hydrogen in the benzene ring, under the directive

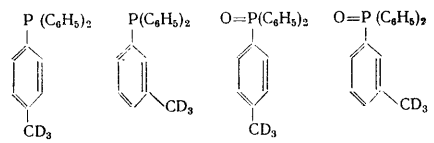
‡ Account must be taken of the fact that the formation of radical-anions from phosphines under the influence of metallic potassium in tetrahydrofuran is complicated by the cleavage of the phosphorus–carbon bond[159].

influence of phosphorus(III), is known, namely the metallation of diphenylphosphine by butyl-lithium, which results in a low yield (5.9%) of the *meta*-lithio-derivative[163]. Metallation of triphenylamine also leads to *meta*-substitution[164,165]. For a more detailed study of the effect of phosphorus-containing substituents on the reactivity of hydrogen atoms and methyl groups in the benzene ring, the authors of the review together with Yakovleva, Shatenshtein, and coworkers[14,167-169] investigated the kinetics of isotope exchange in deuterated triphenylphosphine, triphenylamine, dimethylphenylphosphine, and many other compounds. The partial rate factors for deuterium exchange (f) in liquid ammonia catalysed by potassamide or sodamide (the figures are quoted in brackets) are given below. The analogous data for dimethylaniline are included for comparison[170,171]:



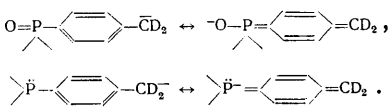
Comparison of the f_n for amines and phosphines indicates significant differences in the electronic effects of nitrogen and phosphorus: in the case of phosphorus the exchange is much faster than in the case of nitrogen. It is interesting that the approximate equality of the exchange rate constants for the *meta*- and *para*-positions of the ring is characteristic not only of phosphines but also of their oxides (1.2×10^{-6} and 0.8×10^{-6} in 1 : 1 t-butyl alcohol–diglyme in the presence of potassium t-butoxide at 120°C), which yet again indicates the similarity of the electronic effects of phosphorus(III) and phosphorus(V).

The electron-accepting properties of the diphenylphosphino-group are shown particularly clearly in the exchange involving the methyl groups of isomeric diphenyltolylphosphines:



(in 1 : 1 t-butyl alcohol–diglyme in the presence of potassium t-butoxide at 120°C).

The exchange rate constants quoted show that the exchange involving the *para*-methyl group is approximately 25 times faster than for the *meta*-methyl group. In the corresponding oxides the difference increases to a factor of 200. These data are evidence of the presence of π-acceptor conjugation in the carbanion or in the transition state arising in the exchange involving diphenyl-*p*-tolylphosphine and its oxide and probably having a structure similar to that of a carbanion:



Thus in the study of hydrogen exchange in aromatic and aliphatic phosphines it proved impossible to detect any signs of $p-\pi$ conjugation.

The electron-accepting properties of phosphorus(III) are observed[14] also when the relative rates of deuterium exchange in methyl groups attached to phosphorus and nitrogen atoms are compared, analogous relations being observed for oxygen and sulphur[172,173] (the exchange was carried out in liquid ammonia in the presence of potassamide, the rate of exchange involving the methyl group of toluene under the same conditions being adopted as a unit):

$C_6H_5N(CH_3)_2$	$(C_6H_5)_2NCH_3$	$C_6H_5OCH_3$
0.0001	0.0002	0.003
$C_6H_5P(CH_3)_2$	$(C_6H_5)_2PCH_3$	$C_6H_5SCH_3$
2	25	10000

2. Reactions Involving the Lone Electron Pair of Phosphorus(III)

The effect of substituents on the reactivity of the lone electron pair of phosphorus(III) has been inadequately investigated quantitatively. A more or less systematic study has been made only of the effect of substituents on the basicity of phosphines. The kinetic studies on the alkylation of phosphines and the addition of sulphur and phenyl azide are few and it is not always possible to arrive at any conclusions concerning $p-\pi$ conjugation.

a. Basicity of phosphines. The effect on this property of electronic and steric factors and of the hybridisation and hydration of the phosphonium cation has been discussed in fair detail by Hudson[41] and Arnett[174]. We shall deal only with problems concerning $p-\pi$ conjugation and shall consider certain studies which were not included in the above reviews.

When comparing the structure–basicity correlations for amines and phosphines, one is struck in the first place by the sharp difference in the effect of $p-\pi$ conjugation on the basicities of these two classes of compounds. During the last ten years a number of correlations have been proposed for amines in which account is taken of the effect on the basicity of electronic factors and solvation[175-179], the lowering of basicity owing to the conjugation of the unshared electron pair with the benzene ring being estimated as equivalent to approximately 3pK units (the agreement between the estimates of this quantity by different workers is not altogether satisfactory). A correlation for phosphines proposed by Henderson and Streuli[180] is analogous to Hall's first correlation for amines[175], where account is taken only of the inductive effects of substituents (Taft's σ^* constants). Tertiary, secondary, and primary phosphines give rise to three linear relations with similar slopes. It is interesting that, in contrast to aromatic amines, aromatic phosphines satisfy this relation. The deviations observed for certain arylphosphines (about 0.5pK unit) might be attributed to a slight $p-\pi$ conjugation, but the deviations are not always of the same sign and probably differ little from the average statistical scatter in the correlation. According to the data of Drenth and Hogervorst[181], the relations of Henderson and Streuli hold satisfactorily also for tertiary alkynylphosphines.

It was shown[182] that in the correlation of the pK_a for phosphines with the σ_{ph} constants for substituents at the phosphorus atom, primary, secondary, and tertiary phosphines give rise to a single linear relation, which is also satisfied by aromatic phosphines. If one remembers that, in terms of the system of σ_{ph} constants, the phenyl group is characterised by an electron-donor resonance effect[183] ($\sigma_I^{ph} = 0.27$, $\sigma_R^{ph} = -0.76$), it becomes clear that on protonation phosphorus in aromatic phosphines exhibits only electron-accepting properties and the lone pair probably does not interact with the π-electron systems of the benzene rings.

By potentiometric titration in nitromethane, Stepanov, Bokanov, and Korolev[16,17,184,185] determined the basicities of a number of ring-substituted diethylphenylphosphines [p-$XC_6H_4P(C_2H_5)_2$], including both electron-donating and electron-accepting substituents. The basicity of these compounds varies linearly with Hammett's σ-constants ($r = 0.9986$ and $s = 0.067$) but not with the σ^- constants, the latter relation being characteristic of substituted anilines. Hence it follows that the electronic effects in the protonation of phosphines are analogous to those in benzoate anions and in this sense differ fundamentally from the effects involving amines. These results also indicate the occurrence of $p_\pi - d_\pi$ conjugation in the protonated phosphine molecule and the insignificance (or absence) of the conjugation of the lone electron pair of the phosphorus atom with the aromatic ring in the molecule of the base.

Goetz and coworkers[186,187] investigated the basicity of phosphines of the same type and also substituted triarylphosphines [p-$XC_6H_4P(C_6H_5)_2$] in 80% alcohol. On the basis of analogous Hammett relations§, they concluded that both $p_\pi - d_\pi$ and $p - \pi$ conjugations occur in phosphines in the ground state. Since the substituents X were exclusively *ortho-para*-directing, the validity of the Hammett relation in this case is evidence only of acceptor conjugation but not of the delocalisation of the lone electron pair. However, on the whole the data for the basicities of substituted arylphosphines are not inconsistent with the hypothesis of the existence of a weak $p - \pi$ conjugation.

b. Alkylation of phosphines. Henderson and Buckler[188] investigated the kinetics of the alkylation of phosphines by alkyl halides. They found that the rate of reaction is determined mainly by inductive and steric factors, although in many cases there are exceptions which have not been fully accounted for. Trialkylphosphines with unbranched substituents (with the exception of the methyl group) and also triaryl and mixed alkylarylphosphines give an imperfect $\lg K - \Sigma\sigma^*$ linear relation, which can nevertheless be attributed to the absence or insignificance of the $p - \pi$ conjugation effect in aromatic phosphines.

c. Addition of sulphur and phenyl azide to aromatic phosphines. The addition of sulphur to substituted triphenylphosphines was investigated by Bartlett and Meguerian[189] and also Goetz et al.[190] The first group of investigators found for a small number of examples (with chlorine and methyl groups as substituents in the benzene rings) that the reaction is of second order and the rate constants are consistent with the Hammett equation (we may note that a similar relation obtains also when the σ^0 inductive constants are employed). Goetz and coworkers established that the reaction is not exactly of second order. Thus definite conclusions concerning the presence or absence of $p - \pi$ conjugation cannot be arrived at on the basis of these data. Nor can one reach conclusions about $p - \pi$ conjugation from studies on the kinetics of the addition of azides to substituted triphenylphosphines recently carried out by Leffler and Temple[191,192].

§ In the correlation of the basicities of aryldiethylphosphines Goetz and coworkers[187] employed averaged Jaffé constants and found that the points corresponding to Cl and Br deviated appreciably from the resulting straight line, to which the authors attributed fundamental importance. It is easy to show that, when McDaniel and Brown's σ constants are employed, a linear relation is obtained with a high correlation coefficient and applies to all the substituents.

C. PROPERTIES OF CERTAIN INDIVIDUAL TYPES OF COMPOUNDS

1. Carboxylic Acid Phosphides

The phosphides of carboxylic acids, containing the group $\diagup\!\ddot{P}-\underset{|}{C}=O$, constitute an interesting system. The presence of the polar carbonyl group and the lone electron pair creates more favourable conditions for $p - \pi$ conjugation than in the $\diagup\!\ddot{P}-\underset{|}{C}=C\diagdown$ systems. These compounds are analogues of carboxylic acid amides, in which there is a very pronounced conjugation of the lone electron pair with the carbonyl group. The study of the chemical and physical properties of carboxylic acid phosphides showed in many cases a difference from the properties of amides, which can probably be regarded as evidence of only a weak $p - \pi$ interaction in this system.

Like carboxylic acid amides, the corresponding phosphides exhibit appreciable acylating properties. According to the data of Tyka and Plazek[193,194], triaroyl phosphides on being heated for many hours with alcohols (140–160°C), give the corresponding esters in quantitative yields. The reaction with aqueous ammonia or aniline results in a quantitative formation of the corresponding amides. Monoacyl phosphides have analogous properties[195,196]. It is interesting that the reverse reactions do not take place. Probably the carbonyl group in phosphides is somewhat more reactive than in amides, but, as stated by Issleib and Priebe[195], there are no fundamental differences between phosphides and amides in this respect.

It is significant that, in contrast to amides, the lone electron pair of phosphorus in monoacyl phosphides retains its reactivity. Thus monoacyl phosphides yield methiodides and form complexes with salts of nickel, mercury, cadmium, and other heavy metals[196,197]. The ease of their oxidation (up to self-ignition) and the capacity to add sulphur and bromine are all evidence of the absence or insignificance of the delocalisation of the lone electron pair of phosphorus[196,197].

Interesting results were obtained in a study of the physical properties of carboxylic acid phosphides. According to Issleib and Löw[196], the ν_{CO} frequencies in amides and phosphides differ little from one another and lie in the range 1640–1680 cm^{-1}, i.e. are much lower than in ketones (Table 14). These results have also been confirmed by Kostyanovskii and coworkers[197-204].

Kostyanovskii and coworkers[197,202,204,205] found that, together with the band indicated above, the spectra of phosphides contain, in contrast to amides, a second band located at a frequency higher by approximately 100 cm^{-1}, which they also attributed to the stretching vibrations of the carbonyl group (Table 15). The presence of two bands was explained by the existence of two stable conformers, the low-frequency band being attributed to the *trans*-conformer (the *trans*-positions of the lone pair and the CO group) and the high-frequency band to the *cis*-conformer. The authors state that the relative intensities of these bands change as a function of the solvent and temperature. Since the conjugation of the lone electron pair and the carbonyl group cannot be achieved for geometrical reasons (the π-electron system of the carbonyl group and the orbital of the lone electron pair do not lie in the same plane), the authors explain the lowering of ν_{CO} by the conjugation of the carbonyl group with the phosphorus d orbitals, which leads to a lowering of the multiplicity of the C=O bond

owing to the reverse polarisation of the carbonyl group with the appearance of a positive charge at the oxygen atom.

$$\rangle\ddot{P}-C=O \leftrightarrow \rangle\ddot{P}=\bar{C}-O^{+}\cdot$$
(I) (II)

Table 14. Comparison of the ν_{CO} frequencies for amides and phosphides $RCOER'_2$ according to the data of Issleib and Löw[196].

Element	ν_{CO}, cm^{-1}			
	R = R′ = alkyl	R = alkyl R′ = aryl	R = aryl R′ = alkyl	R = R′ = aryl
N	1655	1680	1645	1655
P	1650	1670	1640	1655

This treatment is open to objection. The relative contribution of structure II with the unusual polarisation of the carbonyl group to the resonance system should be very small and the insignificant reverse polarisation of the bond, which on the whole has a certain amount of semipolar character ($\bar{C}-\bar{O}$), should lead to an increase and not to a decrease of the amount of double bond character in the carbonyl group and hence to an increase of ν_{CO}. If it is assumed that the multiplicity of the C=O bond is reduced owing to structure (II), then the factors promoting the reverse polarisation should lead to a further decrease of ν_{CO}. Nevertheless ν_{CO} in phosphorus(V) systems of the type $RCOP(O)R'_2$ and $[RCOPR'_2R''X^-]$, where both inductive and mesomeric effects should stabilise resonance structure (II), is higher and not lower.

Table 15. Variation of ν_{CO} in mono- and di-acetophosphides and acetamides[197,202,204].

Formula	ν_{CO}, cm^{-1}		
$CH_3COP(CH_3)_2$	1660	—	1758
$(CH_3CO)_2PCH_3$	1657	—	1758
$CH_3COP(C_6H_5)_2$	1664	—	1758
$CH_3CON(CH_3)_2$		1650	
$(CH_3CO)_2NCH_3$		1700	
$CH_3CON(C_6H_5)_2$		1662	

The decrease of ν_{CO} in amides is due to $p-\pi$ conjugation, which leads to a lowering of the multiplicity of the C=O bond. At first sight it may appear that the lowering of ν_{CO} in phosphides is due to the same phenomenon, but this is contradicted by other chemical and physical data which indicate the absence or insignificance of $p-\pi$ conjugation in systems with phosphorus(III).

For an understanding of the causes of the lowering of ν_{CO} in carboxylic acid phosphides, it is useful to examine the variation of ν_{CO} in carbonyl-containing compounds of the type CH_3COX, where X are atoms or groups containing elements in Pe iods II and III (Fig. 6 and Table 16). One must bear in mind that ν_{CO} does not depend significantly on the mass of the substituents[210] (provided that the mass exceeds 12) and therefore ν_{CO} is determined mainly by electronic factors. For example, it has been shown that ν_{CO} is sensitive to the inductive effects of substituents[211,212].

On passing from carbon to nitrogen, ν_{CO} falls approximately by 60–90 cm^{-1} despite the higher electronegativity of nitrogen, which is due to $p-\pi$ conjugation¶. On further transition to oxygen and fluorine, there is a steady increase of ν_{CO} in conformity with the increase of the inductive and the decrease of the mesomeric effects of these elements. On passing from carbon to silicon, which has a lower electronegativity, ν_{CO} decreases and it was shown that in this case the decrease is caused by a change in the inductive effect of the substituent and not by other factors.

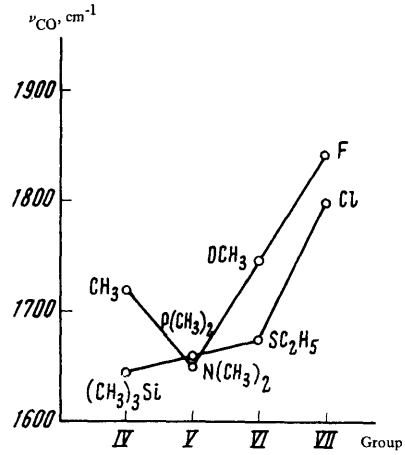


Figure 6. Variation of ν_{CO} in CH_3COX molecules, where X are substituents containing Group IV–VII elements in the Second and Third Periods.

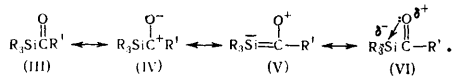
Table 16. Variation of ν_{CO} in CH_3COX molecules (in the condensed phase of solution).

X	ν_{CO}, cm^{-1}	References	X	ν_{CO}, cm^{-1}	References
CH_3	1718	206	$Si(CH_3)_3$	1645	208
$N(CH_3)_2$	1650	204	$P(CH_3)_2$	1660	197,201
				1758	
OCH_3	1747	206	SC_2H_5	1675	209
F	1841	207	Cl	1798	207

In α-silyl-substituted ketones ν_{CO} is reduced approximately by 70 cm^{-1} compared with ν_{CO} in the corresponding ketones without the α-silyl group[208,214–218]. In disilyl-substituted ketones an even greater shift is observed[219]. The replacement of the α-carbon atom of ketones by silicon has a surprisingly powerful effect also on the energy of the electronic transitions[215,218,219], leading to a red shift of the bands in the ultraviolet spectrum and the appearance of a colour in α-silyl-substituted (yellow) and disilyl-substituted (red-violet) ketones, which is not

¶ In amides, where $p-\pi$ conjugation cannot be achieved for geometrical reasons, ν_{CO} does not fall. Thus ν_{CO} = 1756 cm^{-1} for 2,2,6-trimethyl-7-quinuclidone[213].

observed in the ketones having similar structures without the silyl groups. To account for these observations, it was suggested that the lone electron pair of the oxygen atom in the carbonyl group interacts with the silicon *d* orbitals ($n-d$ interaction[215]) and it was postulated that in the excited state the π^* orbitals of the carbonyl group are conjugated with the silicon *d* orbitals[220]. The possible electronic interactions in silyl-substituted ketones can be represented by a set of resonance structures[221] (III–VI):



(III) (IV) (V) (VI)

Examination of this problem with the aid of the simple and extended Hückel methods led to the conclusion[222] that the main reason for the observed influence of silicon and also germanium on the electronic and vibrational spectra is the change in the σ-donor capacity of the substituting α-atom†. This view was confirmed by spectroscopic measurements of the basicity of the carbonyl group in $R_3XCOC_6H_5$.[221] The basicity decreases in the series Si > Ge > C, which is evidence against structures (V) and (VI) in the ground state. Thus it has been shown that the electronegativity of silicon, i.e. its inductive and not mesomeric effect, plays the main role in the changes of ν_{CO}.

For other elements of Period III, with the exception of phosphorus, a lowering of ν_{CO} in the system CH_3COX, analogous to that with silicon, is observed and one may assume that it is caused by a decrease of the inductive effect of X, since the decrease of the mesomeric effect, which takes place on passing to the elements of the Third Period, should lead to an increase of ν_{CO}. This general tendency does not hold only in the case of phosphorus: ν_{CO} in phosphides is reduced compared with ν_{CO} in ketones but not amides. Compared with silicon, there is some increase of ν_{CO} instead of a decrease, as in the case of carbon and nitrogen. One may suppose that the decrease of ν_{CO} for phosphides compared with ketones is caused, by analogy with silicon, by a decrease of electronegativity on passing from carbon to phosphorus and the approximate equality of the ν_{CO} for phosphides and amides is associated with the absence or insignificance of the $p-\pi$ conjugation effect in carboxylic acid phosphides. Issleib and Löw[196] believe that the reason for the decrease of ν_{CO} in phosphides is the polarisability and reduced electronegativity of phosphorus compared with nitrogen.

Two absorption bands, assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition, have been observed in the ultraviolet spectra of phosphides[197,202,204] (Table 17). Compared with amides, which have only one band associated with the $\pi \rightarrow \pi^*$ transition, a bathochromic shift of the absorption maximum should be noted, although it is not as pronounced as in the case of silyl-substituted ketones. A colour is observed only for the phosphides of aromatic and heterocyclic carboxylic acids. The reason for the bathochromic shift is probably the reduced electronegativity of phosphorus.

The introduction of a second acyl group at the phosphorus atom has little effect on the vibrational and electronic spectra (Tables 15 and 17), while in the case of nitrogen a second acyl group increases ν_{CO} and the bathochromic shift in the ultraviolet spectrum[202]. This is associated with a change in the nature of the conjugated system in diacyl derivatives of nitrogen and probably with the absence of $p-\pi$ conjugation in diacyl phosphorus compounds.

Thus the sum total of all the data considered probably indicates the absence from phosphides of $p-\pi$ conjugation analogous to the amide resonance.

Table 17. Ultraviolet spectra of phosphides[197,202,204] and amides[202,224].

Formula	λ, nm (in hexane)		Formula	λ, nm (in hexane)	
	$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$		$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$
$CH_3COP(CH_3)_2$	228.5	347.0	$CH_3CON(CH_3)_2$	195.3	—
$(CH_3CO)_2PCH_3$	220.5	342.0	$(CH_3CO)_2NCH_3$	215.7	—

2. Phosphorus(III) Cyanides

From the standpoint of the conditions for the occurrence of $p-\pi$ conjugation, the $\diagdown\ddot{P}-C\equiv N$ system is more favourable than the $\diagdown\ddot{P}-C=O$ structure. In this case there is no conformational limitation to conjugation. In the discussion of valence angles it was already noted that the C–P–C valence angle in tricyanophosphine is 93.5°, which corresponds to almost complete *s* character of the lone electron pair of phosphorus and hence the absence of capacity for $p-\pi$ conjugation. Therefore the study of the properties of such compounds is of great interest for the conjugation problem.

The chemical properties of phosphorus(III) cyanides have been hardly investigated. Michaelis[225] pointed out that aryldicyanophosphines add chlorine vigorously. Cyanodiphenylphosphine adds sulphur on interaction with $PSCl_3$. Tricyanophosphine forms complexes[227] with aluminium hydride and also with aluminium chloride and bromide. These reactions indicate the retention of reactivity by the lone electron pair despite the powerful inductive effect of the cyano-groups.

As already mentioned, the dipole moment of cyanodiphenylphosphine does not differ from the value calculated assuming additivity[136], which is evidence of either the absence or low contribution of $p-\pi$ conjugation in the molecule. This is consistent also with the vibrational spectra of tricyanophosphine. A correlation[228] between $\nu_{C\equiv N}$ and the electronegativity of the element has been established for the cyanides of various elements. The cyanides of elements with lone electron pairs (fluorine, chlorine, bromine, iodine, and sulphur) give rise to a single linear relation and elements incapable of $p-\pi$ conjugation (carbon, mercury, silicon, and potassium) form another straight line. It is interesting that phosphorus is included among the second group of elements, while sulphur is included among the first. The authors emphasise this finding, which is surprising in their opinion.

The lowering of $\nu_{C\equiv N}$ in phosphorus(III) cyanides compared with alkyl cyanides is probably not caused by conjugation but by the reduced electronegativity of the phosphorus atom. The changes in $\nu_{C\equiv N}$ in $X-C\equiv N$ systems, where X are elements in the Second and Third Periods, are analogous to those described above for the carbonyl compounds CH_3COX (Fig. 7 and Table 18).

† The interaction of the π bond of the carbonyl group with the silicon *d* orbitals is postulated in the excited state[223].

3. Phospholes

The problem of the aromaticity of five-membered phosphorus-containing heterocycles, the so called phospholes, which are the phosphorus analogues of pyrrole, furan, and thiophen, bears a direct relation to problems of $p-\pi$ conjugation.

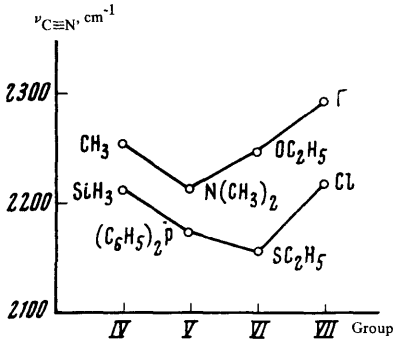


Figure 7. Variation of $\nu_{C\equiv N}$ in X–C≡N molecules, where X are substituents containing Group IV–VII elements in the Second and Third Periods.

A number of polyphenyl derivatives of phospholes were synthesised at the beginning of the 1960's [236-242]. Recently simple representatives of this class of compounds were obtained: 1-phenylphosphole [243] and 1-methylphosphole [244,245]. The study of these compounds [238-241,245-247] showed that, in contrast to aromatic heterocycles, they combine the properties of dienes and saturated compounds of the heteroatom, i.e. phosphines. Phospholes enter into all the reactions characteristic of phosphorus(III) compounds: they are oxidised, add sulphur, and give rise to quaternary phosphonium salts and complexes. On the other hand, pentaphenylphosphole, for example, behaves as a diene forming an adduct with maleic anhydride [238,239].

Table 18. Variation of $\nu_{C\equiv N}$ in XC≡N molecules (in the condensed phase of solution).

X	$\nu_{C\equiv N}$, cm^{-1}	References	X	$\nu_{C\equiv N}$, cm^{-1}	References
CH_3	2254	229	SiH_3	2212 (gas)	233
$N(CH_3)_2$	2212	230	$P(C_6H_5)_2$	2172	196
			$P(CN)_2$	2204	228
OC_2H_5	2245	231	SC_2H_5	2155	234
F	2230 (gas)	232	Cl	2215	235

Tetraphenylthiophen and tetraphenylfuran do not form analogous adducts even under severe conditions. Pentaphenylphosphole forms complexes with iron carbonyls both via the phosphorus atom and via the diene system [238,239]. 1,2,5-Triphenylphosphole forms two types of adduct with acetylenedicarboxylic acid ester—as a diene and as a phosphine with formation of phosphoranes [248].

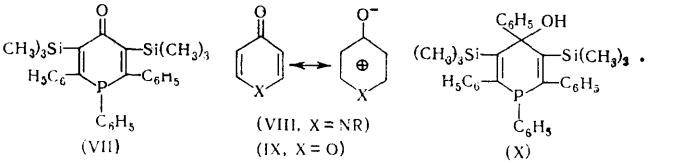
Some evidence for aromaticity was obtained in the study of the simplest phospholes. Thus Märkl and Potthast [243] state that 1-phenylphosphole does not dimerise at 20°C, in contrast to its oxide, and is comparatively difficult to oxidise and combine with sulphur to form a dimeric oxide and sulphide. The NMR spectrum of 1-phenylphosphole resembles that of 1-phenylpyrrole. Quin and coworkers [244,245] enumerate a number of properties, which in their opinion indicate a significant degree of delocalisation of the lone electron pair in 1-methylphosphole: the higher stability of the phosphole compared with that of dienes; the shift of the proton signals in the NMR spectrum towards weaker fields, indicating the existence of a ring current and a similar shift of the signals of the methyl protons; the indication by the ^{31}P NMR spectrum of a reduced electron density at the phosphorus atom compared with alkyldivinylphosphines; the similarity of the ultraviolet spectrum to that of 1-methylpyrrole; the fragmentation on electron impact similar to that of pyrrole and thiophen derivatives; a basicity (0.5) lower by approximately five powers of ten than the expected basicity of methyldivinylphosphine; the absence of reactions with carbon disulphide and nickel chloride. On the other hand, 1-methylphosphole is readily oxidised and forms a phosphonium salt with methyl iodide, which suggests the retention of the reactivity of the lone electron pair of the phosphorus atom. Thus the available data do not allow a final conclusion concerning the presence or absence of aromatic properties in phospholes. However, even if phospholes do exhibit aromatic properties, they are weak and they do not have a significant influence on the overall properties of these heterocycles.

We may note that thermochemical and calculated quantum-chemical data support the existence of aromatic properties in phospholes. According to these results, described in fair detail in Hudson's book [41], phospholes should actually have more pronounced aromatic properties than pyrroles, a result which must naturally be treated with caution‡.

There are no data on the geometry of phospholes. Earlier we pointed out that [12] the valence angles at the heteroatoms in pyrrole, furan, and thiophen are approximately equal to those in the hydrides of the corresponding elements. If this holds also for phosphorus, the valence angles at the phosphorus atom in phospholes should differ only slightly from those in unsubstituted phosphine, i.e. they should not exceed 100° in any case. The predominantly s character which the lone electron pair possesses in this case is in good agreement with the absence of pronounced aromatic properties in phospholes.

4. Phosphacyclohexadienones

Märkl and Olbrich [249] recently synthesised 3,5-trimethylsilyl-1,2,6-triphenylphosphacyclohexa-2,5-dien-4-one (VII), the phosphorus analogue of γ-pyridone (VIII) and γ-pyrone (IX), which are known to have aromatic properties owing to the delocalisation of the lone electron pair of the heteroatom X over the ring:



‡ A planar ring structure was postulated in the calculation.

The phosphacyclohexadienone (VII) does not exhibit the ambident reactivity characteristic of pyrones and pyridones. Thus alkylation and protonation take place at the phosphorus atom and not at the oxygen atom. Compound (VII) enters into reactions characteristic of phosphorus(III) and ketones. The carbinol (X) obtained in the reaction with phenyl-lithium does not form with perchloric acid the corresponding pyrylium salt analogue. All these properties indicate the absence of appreciable delocalisation of the lone electron pair of the phosphorus atom in the phosphacyclohexadienone, although the authors in fact believe that the involvement of the dipolar structure probably should not be entirely excluded.

We shall not consider here the problem of phosphabenzenes, since the lone electron pair of phosphorus does not participate in the conjugated ring system.

V. PROPERTIES OF PHOSPHORUS(III) COMPOUNDS IN AN OPTICALLY EXCITED STATE

A. ULTRAVIOLET SPECTRA OF PHOSPHINES

Examination of the ultraviolet spectra of the simplest chromophoric systems with lone electron pairs of the type CH_3X, where X is a substituent containing elements in Groups V–VII and Periods II and III, shows that the position of the long-wavelength absorption band is inversely related to the electronegativity of the central atom of the substituent X: with increase of the electronegativity of the central atom, the long-wavelength absorption band is displaced towards shorter wavelengths (Table 19). There is a corresponding increase in the excitation energy, which is attributed either to $n \rightarrow \sigma^*$ transitions or, as in some cases, to Rydberg transitions of an electron from lone pair[257-259]. Within the limits of the Second Period, there exists an approximate linear relation between the position of the absorption band and the electronegativity of the central atom (see lines I and II in Fig. 8*a*). On passing from the elements of the Second Period to those of the Third in Groups VI and VII, the absorption bands are displaced towards longer wavelengths (see lines I and II in Fig. 8*b*), in conformity with the decrease of the electronegativity of the elements. However, in Group V the opposite phenomenon is observed—phosphines absorb at shorter wavelengths than amines, which leads to a breakdown of linearity. Thus phosphorus is an exception to the general relation. One may suppose that this blue shift, i.e. the increase of the energy of the long-wavelength transition, in phosphines is associated largely with the lower and not the excited energy level of the lone electron pair, i.e. with the enhanced *s* character of its orbital.

If phosphorus satisfied the above relation, then, according to its electronegativity (2.1 on Pauling's scale), the long-wavelength transition of trimethylphosphine should occur in the region of 240–260 nm instead of the observed wavelength of about 200 nm. The energy difference between the 200 and 250 nm transitions[102] is approximately 28 kcal mole^{-1}. Table 19 lists the parameters of the ultraviolet spectra of other phosphines and, for comparison, data for the corresponding amines. In all cases the long-wavelength transitions of phosphines are displaced towards shorter wavelengths compared with amines, which can probably be regarded as confirmation of the conclusion that the lone electron pair of phosphorus has enhanced *s* character.

Analogous, albeit less pronounced, changes in the position of the long-wavelength absorption bands are also observed for monophenyl derivatives[260-262] (Figs. 8*a* and 8*b*). In this case the long-wavelength transition is of a different type, although the attached element with a lone pair has a significant influence on the nature of the spectrum. The maximum of the long-wavelength absorption band is displaced towards shorter wavelengths on passing from nitrogen to oxygen and fluorine, i.e. on increase of the electronegativity and decrease of the π-donor capacity of the element.

Table 19. Long-wavelength absorption bands of chromophoric systems with lone electron pairs.

Substance	λ_{max}, Å	Solvent	References	Substance	λ_{max}, Å	Solvent	References
NH_3	1942	gas	250	PH_3	1910	gas	253
CH_3NH_2	2150	ditto	250	CH_3PH_2	2010	ditto	253
$(CH_3)_2NH$	2200	»	250	$(CH_3)_2PH$	1890	»	253
$(CH_3)_3N$	2273	»	250	$(CH_3)_3P$	2010	»	253
$(CH_3)_2O$	1840	»	251	$(CH_3)_2S$	2100	alcohol	254
CH_3F	1325	»	252	$(C_2H_5)_2S$	2222	gas	255
				CH_3Cl	1690	gas	256

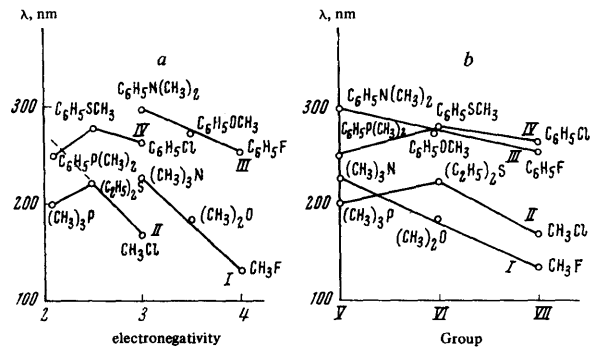


Figure 8. Variation of the positions of the long-wavelength absorption band maxima in the spectra of compounds of the type CH_3X and C_6H_5X (X are substituents with lone electron pairs containing Group V–VII elements in the Second and Third Periods) with Pauling's electronegativity of the central atom of the group X (*a*) and with the positions of the central atom in the Periodic System (*b*).

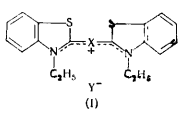
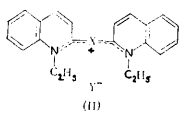
A small bathochromic shift is observed on passing from fluorine to chlorine and from oxygen to sulphur. Again this behaviour breaks down in the case of phosphorus (see Figs. 8*a* and 8*b* and Table 20). According to the general tendency, phosphorus compounds should be characterised by absorption at the longest wavelengths. In fact, however, dimethylphenylphosphine absorbs at shorter wavelengths than the analogous nitrogen and sulphur compounds and, according to the data of Bowden and Braude[261], even fluorine compounds, despite the lower electronegativity of phosphorus compared with those of the above elements. This anomaly in the spectra indicates a significant difference in the structure of the valence shell of phosphorus in

phosphines and possibly also a different type of electronic transition. One may suppose that it is also caused by enhanced *s* character of the lone electron pair of phosphorus.

Table 20. Long-wavelength absorption bands of the monophenyl compounds of certain elements in the Second and Third Periods (in alcohol).

Substance	λ_{max}, nm	References	Substance	λ_{max}, nm	References
$C_6H_5N(CH_3)_2$	309 298	260 261	$C_6H_5P(CH_3)_2$	266.0 251.0	260 261
$C_6H_5OCH_3$	273	260	$C_6H_5SCH_3$	279.0	261
C_6H_5F	254	261	C_6H_5Cl	263.5	260

Table 21. Ultraviolet spectra of cyanine dyes.

Formula	X	Y	λ_{max}, nm	References
 (I)	N	BF_4	376 (CH_3OH)	263
	CH	I	423 (CH_3OH)	263
	P	BF_4	472 (CH_3OH)	263
			478 (C_2H_5Cl)	264
	As	BF_4	491 (C_2H_5Cl)	264
 (II)	N	I	424	268
	CH	I	525	269
	P	ClO_4	5 4 (CH_3OH)	263
	As	BF_4	642 (C_2H_5Cl)	264

It is interesting to note that in those cases where tervalent dicoordinate phosphorus enters into a conjugated system, anomalies of this kind are not observed in the spectra and phosphorus compounds absorb at longer wavelengths than the analogous nitrogen compounds. Thus the phosphamethinecyanines synthesised by Dimroth and Hoffmann[263] have a deeper colour than the corresponding azamethine- and methine-cyanines (Table 21). The analogous arsenic compounds absorb at even longer wavelengths[264]. An approximately linear relation is actually observed between the position of the long-wavelength absorption band maximum and the electronegativity of the central atom (Fig. 9). A bathochromic shift of the long-wavelength absorption maximum relative to the maxima of the corresponding carbon and nitrogen analogues takes place also for other compounds of dicoordinate phosphorus – dibenzophosphorin[265] and 2,4,6-triphenylphosphabenzene[267,269].

Aryl phosphide anions[41], the electronic analogues of aryl sulphides and arenethiols, are also deeply coloured. The appearance at the phosphorus atom of a second lone electron pair with a much more pronounced *p* character than the first leads to a shift of the absorption band towards longer wavelengths in accordance with the electronegativity of phosphorus.

The first data on the ultraviolet spectra of aromatic phosphines were obtained at the beginning of the 1950's. Extensive data have now been accumulated but so far the nature of the observed electronic transitions is not altogether clear.

The introduction of phosphorus(III) into the benzene ring leads to a sharp increase of the absorption intensity in the region of 250–260 nm, which exceeds the usual increase of intensity accompanying the breakdown of the symmetry of the benzene ring, and also to a bathochromic shift of the benzene *K* band. This was first shown by Bowden and Braude[261] for dimethylphenylphosphine and then by other workers[134,135,260,270-276] for other aromatic phosphines. An increase in the number of phenyl groups at the phosphorus atom causes a comparatively small change in the position of the absorption band but leads to an appreciable increase of intensity, which, however, does not rise in proportion to the number of benzene rings[260,271].

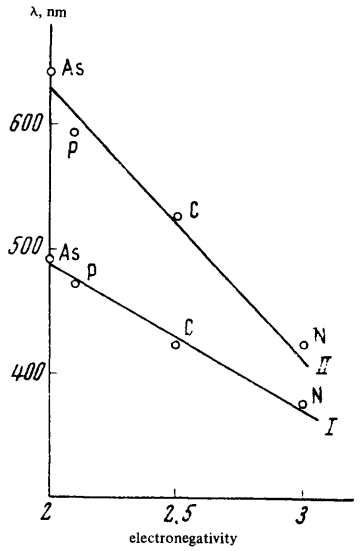


Figure 9. Variation of the positions of the maxima of the long-wavelength absorption bands in the spectra of cyanine dyes of types I and II (Table 21) with Pauling's electronegativity of the central atom.

This effect is shown particularly clearly by aromatic amines. The band intensities are influenced by steric factors. Thus the introduction of a methyl group into the *ortho*-position of 1-phenyl-1-phosphacyclopentane decreases the intensity of the long-wavelength band[270] although not as much as for dimethylaniline[279]. The intense absorption in the region of 250–260 nm is associated with the lone electron pair of phosphorus(III), since this band disappears in the oxidation or formation of phosphonium salts. In phosphorus(V) compounds a low-intensity band with a vibrational fine structure is observed in the same region. We may also note that in phosphorus(V) derivatives there is no progressive increase of intensity on introduction of benzene rings at the phosphorus atom and the rule of additivity holds[271,272].

All these factors are regarded by some workers as evidence for the occurrence of $p-\pi$ conjugation in aromatic phosphines in the ground state. Thus Jaffé[271,272] believed that the ultraviolet spectra of the triphenyl derivatives of Group V elements in the tervalent state indicate

the existence of powerful conjugation between the benzene rings§. This view was supported also by Rao and coworkers[274,275], who assigned the 260 nm band of triphenylphosphine initially to the $n \rightarrow \pi^*$ transition and then to the $\pi \rightarrow \pi^*$ transitions, i.e. to the modified benzene B band, and regarded it as an analogue of the long-wavelength absorption by triphenylamine (297 nm). A similar assignment was made by Schindlbauer and coworkers[276,277], who discussed the spectra of more complex aromatic phosphines. Schiemenz[278] believes that the principal bands in the spectrum of di(cyanoethyl)phenylphosphine and cyanoethyldiphenylphosphine are similar to those associated with the long-wavelength transition of dimethylaniline, although in the case of triphenylphosphine he refrains from a definite assignment of the long-wavelength absorption.

Cullen and coworkers[280,281] stated that triphenylamine is the sole representative of triphenyl derivatives of Group V elements whose benzene rings are conjugated. The spectra of the remaining compounds of the series differ significantly from that of triphenylamine. By mathematical analysis of the spectroscopic data for arylarsines, these workers isolated two long-wavelength maxima, one of which was assigned to the $\pi \rightarrow \pi^*$ electronic transition of the substituted benzene ring on the basis of the influence of solvents and substituents on its position and the other (the principal intense absorption band) was assigned to the $n \rightarrow \pi^*$ transition. This investigation influenced also the interpretation of the ultraviolet spectra of arylphosphines.

Table 22. Ultraviolet spectra of arylphosphines[155].

Formula	$n \rightarrow \pi^*$ transition		$\pi \rightarrow \pi^*$ transition	
	λ_{max}, nm	ϵ	λ_{max}, nm	ϵ
$C_6H_5P(C_2H_5)_2$	252.6	3300	273.2	140
$(C_6H_5)_2PC_2H_5$	251.3	8090	277.8	950
$(C_6H_5)_3P$	261.4	11000	281.7	1250

Shaw et al.[155] made a similar analysis of the ultraviolet spectra of arylphosphines with different numbers of phenyl groups at the phosphorus atom (Table 22). They assigned the principal intense band with a maximum in the region of 250–260 nm to the $n \rightarrow \pi^*$ transition of an electron from the lone pair to a non-bonding orbital of the benzene ring. The low-intensity bands with maxima in the region of 270–280 nm were assigned to the $\pi \rightarrow \pi^*$ transitions of the electrons in the substituted benzene ring. These bands differ little in their positions and intensities from the long-wavelength bands of monosubstituted benzenes, for example toluene[282]: 269 nm (2.4), 262 nm (2.45), 255 nm (2.3), and 249 nm (2.15). This interpretation is equivalent to the acknowledgement of the absence (or insignificance) of $p-\pi$ conjugation in the ground state and the delocalisation of the lone electron pair in the optically excited state. The problem of the presence or absence of weak $p-\pi$ conjugation in the ground state remains open. Shaw and coworkers believe that such weak conjugation is possible in triphenylphosphine on the basis of the long-wavelength displacement of the band associated with the $\pi \rightarrow \pi^*$ transition. The recently published spectra of mono-, di-, and tri-phenylphosphines in the gas phase[283] are interesting in this respect. The spectral curve for triphenylphosphine has a shoulder in the region of 300–310 nm.

A similar interpretation was made by Stepanov and coworkers[184,185] in an examination of the ultraviolet spectra of substituted aryldiethylphosphines. On the basis of the effect of substituents in the aromatic ring and at the phosphorus atom on the position of the absorption maximum, they concluded that the intense long-wavelength band of phosphines is an *R* band ($n \rightarrow \pi^*$ transition) and the $\pi \rightarrow \pi^*$ transition is in the majority of cases masked by this intense absorption.

The interpretation of the long-wavelength band as due to the $n \rightarrow \pi^*$ transition is consistent with the enhanced *s* character of the lone electron pair of phosphorus, and hence with the absence or insignificance of $p-\pi$ conjugation in the ground state and with the physical and chemical properties of aromatic compounds; it explains the "phosphorus" anomaly in the spectroscopic behaviour described above.

The assignment to the $n \rightarrow \pi^*$ transition was made[284] also for the long-wavelength band in the spectra of vinylphosphines in the region of 230–240 nm and the 260–270 nm band for *trans*-diphosphinoethylenes. The absorption in the region of 180 nm observed previously[147] probably refers to the unperturbed band of the $\pi \rightarrow \pi^*$ transition, which usually undergoes a bathochromic shift in the spectra of vinylamines and vinyl sulphides. However, we may note that the above assignments are so far purely qualitative and have not been confirmed by calculations.

B. MOLECULAR REFRACTIONS OF PHOSPHORUS(III) AROMATIC COMPOUNDS

Without considering the problem of the molecular refractions of organophosphorus compounds as a whole, which was recently examined in detail by Tolkmith[285] and partly by other investigators, we shall deal here only with a specific problem—the exaltation of the molecular refractions (ΔMR_D) of aromatic phosphorus(III) compounds. In recent years Kharrasova and Kamai examined the molecular refractions of aromatic phosphorus(III) compounds[290-294].

The replacement of an alkyl group at the phosphorus atom by a phenyl group is always accompanied by the exaltation of molecular refraction, which is regarded as evidence for the conjugation of the lone electron pair of phosphorus with the π-electron system of the benzene ring. ΔMR_D is not constant and depends on the substituents at the phosphorus atom and in the benzene ring and their positions.

The values of ΔMR_D for the simplest mono- and diphenyl compounds of phosphorus(III) are listed in Table 23. In most cases it was compiled using the results of the present authors. For this reason, the ΔMR_D data presented serve merely as an illustration and are not increments to atomic refractions of phosphorus. The smallest exaltations are observed for primary and secondary phosphines and chlorophosphines. When alkyl, alkoxy-, and dialkylamino-groups are introduced at the phosphorus atom, ΔMR_D gradually increases and in the case of the last two groups these value differ significantly from the ΔMR_D for chlorophosphines¶. The introduction of a

§ Subsequently Jaffé apparently abandoned this treatment[273] and stated that the absorption by triphenylphosphine in the region of 260 nm cannot be definitely attributed either to the *B* or *K* band.

¶ Kharrasova and Kamai state[291] that the replacement of chlorine by an alkoxy-group in aromatic compounds of phosphorus(III) does not alter its atomic refraction.

second phenyl group increases the exaltation by 0.5–0.7 cm^{-3}. For triphenylphosphine[299], ΔMR_D = 2.65 cm^3.

The exaltations of disubstituted aromatic compounds (Table 24) depend on the nature of the substituents and their positions in the benzene ring. For *meta*-isomers, ΔMR_D differs only significantly from the sum of the ΔMR_D for the corresponding mono-substituted compounds, whereas for the *para*-isomers they are significantly higher than this sum. In other words, ΔMR_D increases with increasing length of the conjugation chain. The above dependence of ΔMR_D on structure makes it significantly more difficult to devise an additive scheme for the calculation of the molecular refractions of aromatic phosphorus(III) compounds.

Table 23. Exaltation of the molecular refractions of certain mono- and di-phenyl compounds of phosphorus(III) [$C_6H_5PX_2$ and $(C_6H_5)_2PX$].

X	$C_6H_5PX_2$	References	$(C_6H_5)_2PX$	References
H	0.48[a]		1.07[b]	
Cl	0.50	296, 297	1.27[c]	
CH_3	0.77	14	1.26	14
OR	1.20	298	1.83[d]	291
$N(C_2H_5)_2$	1.37[e]		2.08	291

[a]Data of the authors of the review: $C_6H_5CH_2$—b.p. 50–51°C/18 mmHg, n_D^{20} = 1.5812, d_4^{20} = 0.9944; MR_D: found 36.86, calculated 36.38. AR_p (8.97) calculated from the MR_D for primary phosphines with straight-chain alkyl substituents. The constants were taken from Maier's review[295].

[b]Data of the authors of the review: $(C_6H_5)_2PH$—b.p. 120–121°C/4 mmHg, n_D^{20} = 1.6293, d_4^{20} = 1.0744; MR_D: found 61.55, calculated 60.48. AR_p (8.97) calculated from the MR_D for secondary phosphines with straight-chain alkyl substituents. The constants were taken from Maier's review[295].

[c]Data of the authors of the review: $(C_6H_5)_2PCl$—b.p. 141–142°C/5 mmHg, n_D^{20} = 1.6367, d_4^{20} = 1.1904; MR_D: found 66.46, calculated 65.19.

[d]Calculated from MR_D for $(C_6H_5)_2POR$ only.

[e]Data of the authors of the review: $C_6H_5P[N(C_2H_5)_2]_2$—b.p. 121–122°C/4 mmHg, n_D^{20} = 1.5344, d_4^{20} = 0.9731; MR_D: found 80.67, calculated 79.30.

Recently Zaitsev[305] proposed correlation equations for the calculation of ΔMR_D for disubstituted benzenes. As experimental data accumulate, this scheme can probably be used also for organophosphorus compounds.

The absolute values of the above exaltations are fairly high and comparable with those for aromatic amines. However, in order to compare the exaltations of phosphorus and nitrogen compounds, it is probably more reasonable to employ, instead of the absolute value of ΔMR_D, its ratio to the corresponding atomic refraction, which makes it possible to take into account the different polarisabilities of the elements. This ratio, which may be called the relative exaltation, is analogous to the specific refraction of Auwers and Eisenlohr[306] but is more convenient for comparing the analogous compounds of various elements.

The relative exaltations for aromatic phosphines are smaller by a factor of approximately 3 than for aromatic amines. Thus, as regards the breakdown of the additivity of molecular refractions, it would appear that phosphorus(III) compounds may be regarded as typical conjugated systems, although inferior in this respect to aromatic amines. The problem arises of the reliability of the exaltation of molecular refraction as a criterion of the occurrence of conjugation.

Table 24. Exaltation of the molecular refractions of *para*- and *meta*-substituted monophenyl compounds of phosphorus(III).

Compound XC_6H_4Y	ΔMR_D p-XC_6H_4Y	References	ΔMR_D m-XC_6H_4Y	References
$ClC_6H_4PCl_2$	1.10	300	0.67	301
$ClC_6H_4P(C_4H_9\text{-}n)_2$	1.48	300	1.20	301
$ClC_6H_4P(OC_2H_5)_2$	1.56	300	1.31	301
$ClC_6H_4P[N(CH_3)_2]_2$	1.98	300	1.59	301
$NCC_6H_4PCl_2$	1.94	9	1.26	10
$NCC_6H_4P(C_4H_9\text{-}n)_2$	2.94	148	1.98	148
$CH_3OC_6H_4P(CH_3)_2$	1.24	303	0.94	303
$CH_2{=}CHC_6H_4P(OC_2H_5)_2$	2.94	304	—	

Compound XC_6H_4Y	ΔMR_D XC_6H_5	References	ΔMR_D C_6H_5Y	$\Delta MR_D XC_6H_5 + \Delta MR_D C_6H_5Y$
$ClC_6H_4PCl_2$	0.03	302	0.50	0.53
$ClC_6H_4P(C_4H_9\text{-}n)_2$	0.03	302	0.85*	0.88
$ClC_6H_4P(OC_2H_5)_2$	0.03	302	1.20	1.23
$ClC_6H_4P[N(CH_3)_2]_2$	0.03	302	1.37	1.40
$NCC_6H_4PCl_2$	0.83	302	0.50	1.33
$NCC_6H_4P(C_4H_9\text{-}n)_2$	0.83	302	0.85*	1.68
$CH_3OC_6H_4P(CH_3)_2$	0.31	1	0.77	1.08
$CH_2{=}CHC_6H_4P(OC_2H_5)_2$	1.16	1	1.20	2.36

*Data of the authors of the review: $C_6H_5P(n\text{-}C_4H_9)_2$—b.p. 112–113°C/4 mmHg, n_D^{20} = 1.5245, d_4^{20} = 0.9159; MR_D: found 74.34, calculated 73.49.

According to Vol'kenshtein[307], "static exaltation, extrapolated to infinitely long wavelengths, i.e. zero frequencies, is of physical significance". Then the breakdown of the additivity of molecular refractions may be evidence of conjugation in the ground state of the molecule. When the wavelength of the irradiating light is reduced, the exaltation will increase as the irradiation frequency approaches the frequency of the intrinsic absorption by the substance. For example, according to the data of Vasil'ev[308], at infinitely long wavelengths *p*-nitroaniline has an exaltation of 2.7 cm^3, which indicates the occurrence of conjugation in the ground state. The exaltation at 4358 Å reaches 14.85 cm^3. The increase of exaltation is due to the absorption of energy and the transition of some of the molecules to an optically excited state, where the additivity of molecular refractions found from the increments for the ground state should not hold. Certain exaltations are due precisely to this effect and are not associated with conjugation in the ground state. No data are available on the dispersion of the exaltations of molecular refractions for arylphosphines. One cannot exclude the possibility that in this case the exaltations are associated with the intrinsic absorption by the substance and on extrapolation to infinite wavelengths the molecular refractions will be additive. This is confirmed indirectly by the virtual absence of exaltation from vinyl compounds of phosphorus(III),[147] the intrinsic absorption bands of which are displaced towards shorter wavelengths[284].

Recently Zaitsev[309] demonstrated the existence of an approximate correlation between ΔMR_D and the electronic absorption spectra of monosubstituted benzenes.

Thus the exaltation of the molecular refractions of aromatic amines by itself gives no information about the conjugation in the ground state of these molecules. Nor should one forget $p_\pi - d_\pi$ conjugation as a possible cause of exaltation in certain cases.

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The properties of phosphorus(III) compounds discussed, both physical and chemical, have been explained on the hypothesis of an enhanced *s* character of the lone electron pair of phosphorus and to some extent constitute its confirmation. We may note that the nature of the hybridisation of the lone electron pair is fairly rarely taken into account in discussions of $p-\pi$ conjugation†, even in certain quantum-chemical studies[283,312]. Usually it is postulated that any lone electron pair is capable of $p-\pi$ conjugation to some extent, which depends on the position of the element in the Periodic System. Much attention has been devoted to the dependence of conjugation on steric factors (various types of non-coplanarity of the *p*-orbital axes), while the effect of changes in valence angles and of the hybridisation of the lone electron pair is rarely taken into account, although it is known that the *s* orbital does not form a bond with the p_Z orbital[45]. We believe that the chemistry of phosphorus(III) has shown that the hybridisation of the lone electron pair is a significant factor influencing the $p-\pi$ conjugation and the properties associated with it. Probably the geometry of the molecule always affects the conjugation not only because of a change in the relative distribution of the overlapping orbitals but also via a change in the very nature of the orbitals and the suggested hypothesis is probably more general and of wider significance than for the chemistry of phosphorus alone.

The problem naturally arises whether it is possible to predict on this basis cases in the chemistry of other elements where the lone electron pair of the atom loses the capacity for $p-\pi$ conjugation by virtue of its enhanced *s* character. The necessary conditions for the observation of this effect are the presence of only one lone electron pair and the closeness of the valence angles at the heteroatom to 90°C. On the basis of data for the valence angles in the hydrides of various elements (see p. 181, Table 1), one may note in what cases the absence of the capacity for $p-\pi$ conjugation in the lone electron pair of the atom is to be expected.

A sharp decrease of valence angles is observed on passing from elements in the Second Period to those in the Third Period within the limits of Groups V and VI. As shown above, in Group V this change in angles is accompanied by a change in directive influence. Since the valence angles in the hydrides of arsenic and antimony steadily decrease, approaching 90°, one may suppose that the lone electron pairs of these elements will also lack the capacity for $p-\pi$ conjugation. In Group VI, transition from the Second to the Third Period is not accompanied by a change in the type of directive influence of the central atom owing to the presence of two lone electron pairs. However, in the case of the tricoordinate state of Group VI elements, for example in 'onium compounds, the pattern of the changes in directive influence should be the same as in Group V elements. An analogous change in directive influence may also be expected for the tricoordinate state of Group IV elements, i.e. in the case of their anions, and the anions of silicon and its analogues should differ sharply in their electronic influence from carbanions.

The experimental data for certain properties (the type of directive influence of the central atom, basicity, and configurational capacity) of π-electron systems containing Group IV–VI elements in the tricoordinate state were recently examined by the present authors[313]. They agree with the hypotheses put forward. Here we shall recall only studies dealing with problems of directive influence and certain others which had not been dealt with previously.

Together with Lobanov, Kamai, and Chadaeva, the authors of the review[314] showed that arsenic, the closest analogue of phosphorus in the Group, resembles the latter in its electronic influence and its lone electron pair also lacks the capacity for $p-\pi$ conjugation. This is also indicated by the data of Kostyanovskii and coworkers[315].

It is interesting that the 100% *para*-directing effect in the nitration of a triphenyloxonium salt, which is unusual for 'onium compounds, observed by Nesmeyanov and coworkers[316] follows logically from the proposed hypothesis. The change in the type of directive influence on passing from oxonium to sulphonium salts is analogous to the inversion of directive influence on passing from nitrogen to phosphorus. Triphenyloxonium salts are electronic analogues of triphenylamine and probably have similar molecular geometry and hence their lone electron pair is almost entirely of *p* type‡. The lone electron pair of triphenylsulphonium salts, the electronic analogues of triphenylphosphine, probably has an appreciable amount of *s* character and hardly participates in $p-\pi$ conjugation. Finally, one must also bear in mind *d* orbitals with likewise promote the *meta*-directing effect. A similar *meta*-directing effect is observed with selenonium salts[317].

Some data whereby the hypotheses put forward may be checked are provided by five-membered diene heterocycles. Anionic cyclic systems containing Group IV elements should not have aromatic properties with the exception of the cyclopentadienide anion, which is derived from an element of the Second Period. The same applies also to Group V elements, nitrogen being an exception in this case. Group VI elements, which have two lone electron pairs, should all form aromatic heterocycles without exception. In the tricoordinate state, the same Group VI elements will not form aromatic heterocycles, with the exception of oxygen.

The facts known at present do not contradict the above hypotheses. We shall not dwell on the widely known examples of aromatic heterocycles—pyrrole, furan, thiophen, selenophen, and the cyclopentadienide anion. According to the hypotheses, the ring compounds with sulphur(III) (thiophen oxide), which is an unstable reactive diene, has no aromatic properties, although it does have a lone electron pair[318]. In this respect, the study of oxonium salts of furan, which should be aromatic, is of very great interest. As already stated, phospholes do not have very marked aromatic properties. However, one may assume that, in the form of phosphide anions, phospholes will behave as aromatic systems analogous to the

† These problems are partly dealt with in monographs[102,310] and certain papers[75,311].

‡ The *meta*-directing effect observed in the nitration of 2-phenylpyrylium salts[3] is not inconsistent with the *para*-nitration of triphenyloxonium salts, since in the first case the lone electron pair is probably located in the plane of the aromatic ring and is not conjugated with the benzene ring.

cyclopentadienide anion. The study of the silacyclopentadienide anion, the silicon analogue of the cyclopentadienide anion, has so far not provided a definite answer to the question of its aromaticity[319].

Another range of phenomena is closely associated with the problems discussed. Indirect evidence for the geometry of silicon(III) [Si (IV) tricoordinate Si? (Ed. of Translation)] compounds and hence for the type of directive influence of the negatively charged atom is provided by the inability of silicon to form a double bond[320]. We believe that this demonstrates the closeness of the valence angles in tricoordinate silicon compounds to 90°, the predominantly *s* character of the free silicon orbital, and hence the absence of $p-\pi$ conjugation in these systems (positively or negatively charged).

The forced decrease of the valence angles of carbon and nitrogen leads to analogous phenomena. This concerns all cases associated with Bredt's rule—the impossibility of the existence of double bonds or resonance interactions at the bridgeheads of bicyclic systems: the absence of amide resonance from quinuclidones[321] and the much lower basicity of dehydroquinuclidine and analogous compounds compared with the corresponding saturated compounds[322,323], the absence of resonance stabilisation from bicyclic carbanions with the charge at the bridgehead[324], etc. The impossibility of π-electron interactions in all such cases is due not only to the unfavourable geometrical disposition of the corresponding orbitals, which is usually emphasised, but also to the enhanced *s* character of the orbital at the bridgehead. The closeness of the average valence angle at the bridgehead in bicycloheptane systems to 100° has been pointed out by Sim[325].

Returning to phosphorus, we may note that the problem of the possibility of detecting $p-\pi$ conjugation in certain special cases is of great interest. We believe that there are three ways whereby phosphorus(III) systems may be formed in which $p-\pi$ conjugation is possible: (1) optical excitation of molecules; (2) the formation of a cationic centre in the α-position relative to phosphorus(III): (3) a "forced" change in the valence angles of the phosphorus atom by the introduction of bulky substituents or by the formation of cyclic structures.

Analysis of the ultraviolet spectra of aromatic phosphines leads to the extremely reasonable conclusion that in an optically excited state $p-\pi$ conjugation may occur. Its observation requires a study of the properties of optically excited molecules. One cannot exclude the possibility that the presence in the molecule of a powerful electron-accepting centre, for example a carbonium ion, leads to the delocalisation of the lone electron pair of phosphorus(III). Evidence for this is provided by the study of the reaction of tri(chloromethyl)phosphine which we investigated[326]:

$$\rangle\ddot{P}CH_2Cl \rightarrow \left[\rangle P^{+}\cdots CH_2\right] \xrightarrow{H_2O} \rangle P(=O)-CH_3 .$$

Hydrolysis and reaction with alkoxides lead to the reduction of the chloromethyl group and the oxidation of phosphorus(III) and not simple substitution. This reaction, which we called "pseudoallyl rearrangement", probably indicates some delocalisation of the lone electron pair in the transition state.

The third way, involving a change in the valence angles at the phosphorus atom, has at present not been investigated at all, although isolated data show that the desired results may be obtained by this procedure. Mark and van Wazer[327] showed that the lone electron pair of tri-t-butyl phosphite has an enhanced reactivity, which they explained by an increase of the valence angles and of the *p* character of the lone electron pair. Subsequently this was confirmed[328] by the ^{31}P NMR method. Arbuzov and Zoroastrova[329], who synthesised a number of cyclic phosphites, noted that seven- and eight-membered phosphorochloridites ignite spontaneously in air, in contrast to the remaining members of the series. This finding has received no explanation. If one bears in mind that, according to X-ray diffraction data[330-335], the valence angles in 8–12-membered rings exceed the tetrahedral value (for example, in cyclononylamine hydrobromide[331] the C–C–C angles are in the range 111–124°), this anomaly can be understood. Probably an increase in the valence angles at the phosphorus atom leads to an increase in the amount of *p* character of the lone electron pair and an increase in its reactivity.

ADDENDA

During the preparation of this manuscript for the press, certain studies were published which the authors feel it necessary to include in the review. Wherever possible the additional data were introduced into the main text. In addition, three new small sections have been written, supplementing the sections on "The Basicity of Phosphines", "Phospholes", and "The Properties of Certain Individual Types of Compounds".

The barrier to the inversion of 1-isopropyl-2-methyl-5-phenylphosphole[336], determined by the NMR method, proved to be very low (ΔG_{25} = 16 kcal mole^{-1}), in contrast to tertiary phosphines for which the inversion barrier is 29–36 kcal mole^{-1}. The authors explain the lowering of the barrier by the energy gain due to the delocalisation of electrons in the transition state of the inversion process.

Proton Affinity of Unsubstituted Phosphine in the Gas Phase

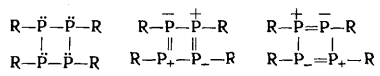
In contrast to ammonia, amines, and substituted phosphines, unsubstituted phosphine is known[41,174] to have an extremely low basicity in water (pK_a = −8 or −14), which Gibbs[337] explained by the almost complete *s* character of the lone electron pair of phosphorus and hence high rehybridisation energy from the p^3 to the sp^3 state in the phosphonium cation. On the basis of calculations using the Born–Haber cycle, Wendlandt[338] concluded that, despite the low accuracy of the values obtained, in the gas phase ammonia and phosphine differ little in their proton affinity (proton affinity is understood as the enthalpy, with the sign reversed, of the reaction $B + H^+ = BH_4^+$).

This led to another view, according to which the low basicity of unsubstituted phosphine in water is a consequence of the low solvation energy of the phosphonium ion[41,338,339]. Subsequently new estimates of the proton affinity of unsubstituted phosphine were published[340,341] (153 and 194.4 kcal mole^{-1}), which differed from Wendlandt's results (209 kcal mole^{-1}). According to the latest data[342] obtained by ionic cyclotron resonance, the proton affinity of unsubstituted phosphine is 185 ± 4 kcal mole^{-1}, which is smaller by 22 kcal mole^{-1} than the proton affinity of ammonia[343] (207 ± 3 kcal mole^{-1}). This value is comparable with the difference between the basicities of phosphine and ammonia in water (23–32 kcal mole^{-1}). Hence

it follows that solvation probably does not play a major role in the difference between the basicities of unsubstituted phosphine and ammonia in water.

Conjugation in Compounds with a P–P Bond

The problem of the possible aromatic properties of cyclopolyphosphines $(RP)_n$ ($n = 4$, 5, or 6) owing to the delocalisation of the electrons in the lone pairs of the phosphorus atoms and represented by the resonance structures



has been discussed in the literature[344,345]. This hypothesis was put forward[346,347] to account for the long-wavelength absorption in the ultraviolet spectra of cyclopolyphosphines (275–290 nm for alkyl derivatives), which is absent from the spectra of tertiary phosphines, and also for the low basicity of cyclopolyphosphines[347] ($pK_a < 1$) compared with phosphines ($pK_a = 2-10$). To confirm this treatment of the ultraviolet spectra, a quantum-chemical calculation was carried out[346].

Analogous evidence (ultraviolet spectra[348,349] and dipole moments[350]) was adduced in support of the existence of a partial double bond character in diphosphines in the ground state and certain polyphosphine heterocycles[351]. Some chemical properties of polyphosphines have also been explained[344,345,352] by the conjugation of the lone electron pair of phosphorus with the d orbitals of an adjacent phosphorus atom.

The valence angles at the phosphorus atom have been determined for trifluoromethyl[353,354], phenyl[355,356], and cyclohexyl[357] derivatives of tetra- and penta-phosphines. In most cases they do not exceed 100°. This implies that the lone electron pairs of phosphorus atoms are predominantly of s type and their conjugation with the d orbitals of phosphorus (the formation of a π bond) can hardly influence significantly the properties of cyclopolyphosphines in the ground state. We believe that the observed long-wavelength shift can be due both to $p_\pi - d_\pi$ conjugation in the optically excited state and to differences between the properties of the P–P (polyphosphines) and C–P (tertiary phosphines) σ bonds i.e. the difference between the electronegativities of carbon and phosphorus (see the section "Carboxylic Acid Phosphides"). The operation of the latter factor is supported, in particular, by the bathochromic shift in the ultraviolet spectra of diphosphine disulphides[349] (compared with trialkylphosphine sulphides), which cannot be accounted for by conjugation. The low basicity of cyclopolyphosphines may be associated with the enhanced s character of the lone electron pairs of phosphorus. The approximate equality of the P–P bond lengths, which are independent of the valence state of phosphorus and of the nature of groups attached to it[357], is also evidence against conjugation in the ground state.

Recently, in a discussion of the causes of the weak nucleophilic properties of the lone electron pair of phosphorus in trisilylphosphine, the hypothesis was put forward[358] that the lone s electron pair of phosphorus forms a σ bond with the d orbital of silicon located along the Si–P bond axis (for example the $s-d_{z^2}$ σ bond). The hypothesis of additional σ bonding, rather than the π bonding, discussed above, may serve as an alternative explanation of the properties of compounds with a P–P bond.

Thus the properties of polyphosphines may be understood in terms of hypotheses other than that of $p_\pi - d_\pi$ conjugation in the ground state, which is difficult to reconcile with the extensive experimental data on the properties of phosphorus(III) compounds§.

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§ Added in proof. The weaker nucleophilic properties of the lone electron pair of phosphorus in triethyl phosphorothioite can be understood similarly; the hypothesis of the d hybridisation of the lone electron pair of phosphorus was recently put forward to account for it[361].

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