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THE ELECTRON INFLUENCE OF SUBSTITUENTS CONTAINING TRIVALENT PHOSPHORUS

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Abstract—The groups containing trivalent phosphorous belong to the second-kind substituents although they possess a lone electron pair. β-Orientation of piperidine addition to vinyl-P^{III}-compounds, ionization constants of phosphorus-substituted benzoic acids or phenols as well as protophylic hydrogen exchange reaction in tertiary phosphines are all indicative of this fact. We determined the σ-Hammett- and σ^--constants and calculated σ_I- and σ_R-constants for Ph_2P-, $Ph_2P(O)$-, $Ph_2P(S)$- and Ph_2N-groups. The results show either no or minor p-π-conjugation effect and the presence of acceptor conjugation. The lone electron pair of trivalent phosphorus displays a weaker p-π-conjugation than those of other third period elements. The reason for this may possibly be an increased s-character on a lone pair of phosphorus electrons, which agrees with the values of valence angles in P^{III}-compounds.

INTRODUCTION

BY ANALOGY with nitrogen and other elements having a lone pair of electrons, and taking into account the location of phosphorus in the periodic system, the groups containing trivalent phosphorus are usually considered to be *ortho–para*-orientating substituents,[1] i.e. they are assumed to exhibit π-donor effect, which should be maximal among the elemnts of the third period.

$$R^2P > RS > Cl.$$

Only a minor drop in π-donor effect compared with that for nitrogen is to be expected, and the difference should be similar to that between oxygen and sulphur.

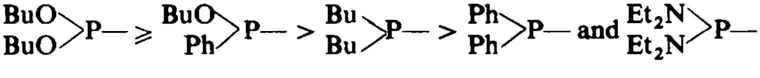
The present paper gives the experimental results of this problem.

Addition orientation of piperidine to vinyl-P^{III} *compounds.* When nucleophilic reagents add to vinyl compounds of pentavalent phosphorus, β-orientation occurs irrespective of the type of group attached to phosphorus.[2–4]

Unexpectedly, the same type of orientation also occurs for vinyl-P^{III} compounds although their reactivity is significantly lower than that for P^V-compounds.[3,5] The addition of piperidine occurs, for example, only after prolonged heating of the reactants at 140–160°.

$$>PCH = CH_2 + C_5H_{10}NH \rightarrow >PCH_2CH_2NC_5H_{10}.$$

Qualitatively, vinyl-P^{III} compounds of the type $X—CH{=}CH_2$ form the following series according to their reactivity towards piperidine.

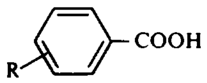


$$\begin{smallmatrix}BuO\\BuO\end{smallmatrix}\!>\!P— \geqslant \begin{smallmatrix}BuO\\Ph\end{smallmatrix}\!>\!P— > \begin{smallmatrix}Bu\\Bu\end{smallmatrix}\!>\!P— > \begin{smallmatrix}Ph\\Ph\end{smallmatrix}\!>\!P— \text{ and } \begin{smallmatrix}Et_2N\\Et_2N\end{smallmatrix}\!>\!P—$$

(the listed substituents are X).

The most active are vinylphosphonites and vinylphenylphosphinites which react with piperidine without catalysts. Piperidine hydrochloride accelerates the reaction but does not change the orientation. The substitution of both BuO groups for Ph groups diminishes the activity of the double bond so that with or without an acid catalyst the addition was not observed.* In the case of more the electropositive Bu_2P group, the addition with piperidine hydrochloride still occurs, probably due to the formation of dibutylvinylphosphine hydrochloride. The addition was not observed for tetraethyldiamidovinyl phosphonite with an acid catalyst, however, diethylamine showing weaker reactivity was used as the amine. Therefore, trivalent phosphorus orientates the addition in the same manner as silicon having no lone pair of electrons which show β-orientation.[6, 7] Later Peterson[8] observed β-orientation for butyl lithium acting on vinyl phosphines. β-Addition under the action of butyl lithium which is a strong nucleophile was observed also for phenylvinylsulphide.[9]

TABLE 1. THE CONSTANTS FOR THE STUDIED SUBSTITUTED BENZOIC ACIDS



R	M.P. °C (solvent)	Published data M.P., °C	Neutralization equivalent	
			Measured	Calculated
p-Ph_2P	156–157	156,[13] 156–158,[14]	305·0	306·3
	(gl. AcOH)	156–158,[15] 156–157[16]	305·6	
m-Ph_2P	159–160·5	157,[13] 157–160[14]	304·6	
	(aqueous alcohol)		305·4	
p-Ph_2N	201·5–202·5	202-203[17]	288·3	289·3
	(gl. AcOH)		289·3	
m-Ph_2N	187–188	186[17]	287·7	
	(gl. AcOH)		289·0	
p-$Ph_2P(O)$	268–269·5	270–271,[14] 273–274[15]	320·8	322·3
	(aqueous dioxan)	270–272,[16] 263–265[18]	321;5	
m-$Ph_2P(O)$	232–232·5	232,[13] 230–232[14]	321·8	
	(alcohol)	234–236[18]	322·0	
p-$Ph_2P(S)$	177–178·5	181–182,[15] 180–182[16]	337·8	338·4
	(EtOAc-hexane)	153–155[15]	337·6	
m-$Ph_2P(S)$	171–172		337·3	
	(EtOAc-hexane)		338·6	

When considering the β-orienting effect of P^{III}-containing groups one should remember that their total electron effect may be a sum of three effects—induction, p-π- and p_π–d_π-conjugation. The inductive effect of phosphorus seems to be close to zero since the electronegativity of hydrogen and phosphorus are equal according to Pauling (2,1). The inductive effect of a phosphorus-containing group depends, in general, on the substituents bonded to phosphorus: for $(BuO)_2P$ and Ph_2P groups weak—I effects may be supposed, for Bu_2P group—a weak +I-effect.

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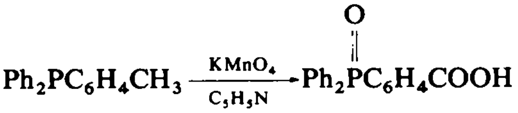
* The addition product could be obtained in the presence of catalytical amounts of sodium. (Results obtained by I. G. Malachova).

β-Orientation of non-catalytical addition suggests either the absence or negligibility of the π-donor effect for trivalent phosphorus. Its electron-accepting influence upon the polarization of the double bond in the starting molecule, or stabilization of transition state by trivalent phosphorus are probably caused by p_π–d_π-conjugation and by inductive effect. The acid-catalysed β-addition may occur due to the formation of corresponding phosphonium salt on account of acid-base equilibrium between amine hydrochloride and vinyl-P^{III} compound.

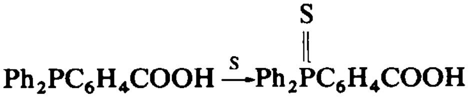
These results show that only a small, if any, p-π-conjugation is present in trivalent phosphorus compounds. This conclusion agrees with data on the intensity of valent C=C-vibrations in the Raman spectra of vinyl and allyl P^{III} compounds.[10] The increase in integral intensity of the double bond line, which is the indication of p–π-conjugation, was not observed in the spectra. This increase is clearly defined for nitrogen and sulphur vinyl compounds while it was not observed for vinyl silanes. As to the spectral properties of the double bond, vinyl-P^{III} compounds are not very different from alkenes-I. The chemical as well as spectral properties of vinyl-P^{III} compounds show that they resemble vinyl compounds of silicon rather than those of nitrogen or sulphur.

Ionization constants for phosphorus-substituted benzoic acids. In order to study quantitatively the electron effects of phosphorus-containing groups, we investigated their influence upon the strength of corresponding substituted benzoic acids. We synthesized some *meta*- or *para*-phosphorus-containing benzoic acids[11, 12] according to the scheme:

$$Cl_2PC_6H_4CN \xrightarrow[(2)\ H_2O,\ HCl]{(1)\ Ph\ MgBr} Ph_2PC_6H_4COOH$$



$$Ph_2PC_6H_4CH_3 \xrightarrow[C_5H_5N]{KMnO_4} Ph_2\overset{\overset{O}{\|}}{P}C_6H_4COOH$$



$$Ph_2PC_6H_4COOH \xrightarrow{S} Ph_2\overset{\overset{S}{\|}}{P}C_6H_4COOH$$

meta- and *para*-Diphenylamino benzoic acids were also obtained for comparison.

$$IC_6H_4COOCH_3 \xrightarrow[(2)\ KOH]{(1)\ Ph_2NH} Ph_2NC_6H_4COOH$$

The constants of the synthesized compounds are listed in Table 1.

The apparent ionization constants for these acids in aqueous alcohols 1:1 and 1:4 (v/v) were determined by potentiometric titration with a glass electrode (Table 2). In these solvents the ionization constants necessary for the calculation of pK_0 and ρ-parameters in the Hammett equation were determined for several substituted benzoic acids (Table 3). The correlation equations (Table 3) were derived using the constants σ given by McDaniel and Brown.[23]

The correlation equations were used to calculate σ-Hammett constants for Ph_2P, Ph_2N, $Ph_2P(O)$ and $Ph_2P(S)$ groups (Table 2). The σ-values obtained from the ionization constants in aqueous alcohols 1:1 and 1:4 agree very closely. Using the ionization constants for *meta*- and *para*-isomers in aqueous 1:1 alcohol we have obtained rough σ_I- and σ_R-values by the Taft-Lewis and Roberts-Jaffe procedure.[24]

The positive σ-constants indicate the acceptor nature of phosphorus-containing

TABLE 2. IONIZATION CONSTANTS (pK_a) FOR PHOSPHORUS-SUBSTITUTED BENZOIC ACIDS RC_6H_4COOH AND σ-, σ_I- AND σ_R-CONSTANTS FOR THE SUBSTITUENTS

	Aqueous alcohol $1:1^{*,a}$				Aqueous alcohol $1:4^a$				b	b
	pK_a	$\frac{K_{meta}}{K_{para}}$	σ	$\sigma_p - \sigma_m$	pK_a	$\frac{K_{meta}}{K_{para}}$	σ	$\sigma_p - \sigma_m$	σ_I	σ_R
p-Ph_2P	5·39	0·76	0·19	0·08	6·34	0·66	0·18	0·11	0·05	0·14
m-Ph_2P	5·51		0·11		6·52		0·07			
p-Ph_2N	6·10	2·18	−0·29	−0·22	7·10	2·13	−0·30	−0·21	0·11	−0·40
m-Ph_2N	5·77		−0·07		6·77		−0·09			
p-$Ph_2P(O)$	4·88[c]	0·58	0·53	0·15	5·82	0·57	0·52	0·16	0·27	0·26
m-$Ph_2P(O)$	5·11[d]		0·38		6·07		0·36			
p-$Ph_2P(S)$	4·97[e]	0·54	0·47	0·18	5·95	0·60	0·43	0·14	0·15	0·32
m-$Ph_2P(S)$	5·24		0·29		6·17		0·29			

[a] v/v, 25°.

[b] Calculated using the data for aqueous alcohls, 1:1.

[c] Published data:[18] $pK_a = 4·79$

[d] Published data:[18] $pK_a = 5·01$

[e] The improved pK_a-value.

TABLE 3. IONIZATION CONSTANTS (pK_a) FOR THE SUBSTITUTED BENZOIC ACIDS RC_6H_4COOH AT 25° AND THE σ-HAMMETT CONSTANTS FOR THE SUBSTITUENTS R

R	*p*-MeO	*p*-Me	H	*p*-Cl	*p*-Br	*m*-Cl	*m*-Br	*m*-NO$_2$	*p*-NO$_2$	Equations
pK_a aqueous alcohol 1:1										$\lg K_a = -5{\cdot}67 + 1{\cdot}480\,\sigma$ $\pm 0{\cdot}05;\ \sigma = 3{\cdot}80 + 0{\cdot}670$
Our data	6·01	5·93	5·72	5·32	5·27	5·17	5·15	4·61	4·47	$\lg K_a \pm 0{\cdot}03;\ r = 0{\cdot}996$
Published data	6·07[20]	5·80[19]	5·64[19]	5·20[19]						
	6·12[21]	5·94[20]	5·75[20]		5·35[20]			4·66[20]	4·53[20]	
		6·00[21]	5·80[21]							
			5·71[22]							
			5·72[18]					4·51[18]	4·47[18]	
			5·44[a]					4·32[a]	4·15[a]	
pK_a aqueous alcohol 1:4										$\lg K_a = -6{\cdot}63 + 1{\cdot}554\,\sigma$ $\pm 0{\cdot}05$ $\sigma = 4{\cdot}23 + 0{\cdot}639$
Our data	7·08	6·85	6·66	6·23	6·19	6·12	6·05	5·52	5·41	$\lg K_a \pm 0{\cdot}03;\ r = 0{\cdot}996$
Published data		6·73[19]	6·61[19]	6·13[19]		6·06[19]				
			6·30[a]					5·17[a]	5·00[a]	
σ	−0·268	−0·170	0	0·227	0·232	0·373	0·391	0·710	0·778	

[a] The measurements were carried out using a quinhydrone electrode.[19]

groups. The inductive effect of Ph_2P groups is weak ($\sigma_I = 0{\cdot}05$) which agrees with phosphorus electronegativity. The groups containing pentavalent phosphorus show larger inductive constants. The Ph_2N group exhibited greater inductive effect than Ph_2P group, which is consistent with the electronegativity difference between nitrogen and phosphorus (3·0 and 2·1, respectively, according to Pauling). The resonance effects for phosphorus-containing groups, especially for the Ph_2P group, are of great interest. The latter, unlike the Ph_2N group appeared to be in π-electron-acceptor group despite the presence of a lone pair of electrons. Ph_2N group is a π-donor substituent although its mesomeric effect is slightly weaker compared to that of Alk_2N groups. The resonance effects of the substituents with pentavalent phosphorus are positive and far exceed in value that of the Ph_2P group.

These results were later confirmed by other authors. The data on the σ-Hammett constants available for several phosphorus-containing substituents (mostly for *para*-substituents) are given in Table 4. No chemical data on *meta*-substituents with trivalent phosphorus are presently available. Data obtained by Schiemenz[25, 26] for *para*-phosphorus containing group* are nearly the same as ours. For the p-$Ph_2P(O)$ group Monagle, *et al.*,[18] also give a value close to these constants. Somewhat different σ-values were obtained by Baldwine, *et al.*,[16] from the ionization constants for phosphorus-substituted benzoic or aryl phosphinic acids in aqueous tetrahydrofuran. They are lower in value for all phosphorus-containing groups, probably, because of the solvent. Positive but higher σ_p-values for the Ph_2P group were obtained from the reactivity data of p-diphenylphosphinostyrene in its copolimerization with styrene and methyl metacrylate.[27] σ-constants for m-$Ph_2P(O)$ were obtained by Monagle, *et al.*,[8] and also by Bott, *et al.*[28] These values differ insignificantly from our data.

TABLE 4. σ-HAMMETT CONSTANTS FOR THE PHOSPHORUS-CONTAINING SUBSTITUENTS

Substituent	σ					
p-Ph_2P	0·19[a];	0·19[26];	−0·01[16];	0·3[27];	0·5[27]	
m-Ph_2P	0·11[a]					
p-$Ph_2P(O)$	0·53[a];	0·50[26];	0·553[18];	0·44[16];	0·65[27];	0·0[27]
m-$Ph_2P(O)$	0·38[a];	0·422[18];	0·434[18];	0·485[28]		
p-$Ph_2P(S)$	0·47[a];	0·49[26];	0·28[16];	0·65[27];	0·45[27]	
m-$Ph_2P(S)$	0·29[a]					

[a] Our data for aqueous alcohol (1:1).

Alk_2P groups are of considerable interest. Presently only the σ_p-value for the Et_2P group (0·03) determined by Stepanov, *et al.*,[29] from the basicity of tetraethylparaphenylenediphosphine is available. This value differs significantly from the σ_p-value for the Me_2N group (− 0·83). A number of σ-Hammett constants for phosphorus-containing substituents were obtained using the spectral methods (IR spectra,[26, 30] NMR-C^{13} spectra[31] and NMR-F^{19} spectra[32, 35]). In general, these data agree with the results obtained by chemical methods. Rakshys *et al.*[33, 34]

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* The improved values of the constants by Schiemenz are true.[26]

and Johnson and Jones[35] calculated σ_I and σ_R-constants for phosphorus-containing groups using NMR-F^{19} spectra for *meta*- and *para*-phosphorus-substituted fluorobenzenes. It follows from these results, that the inductive effect dominates in the total electron effect of the substituents (for example $\sigma_I = 0{\cdot}17$ and $\sigma_R = -0{\cdot}01$ for Ph_2P group). Therefore, there is a certain amount of discrepancy between the chemical data and NMR-F^{19} results.

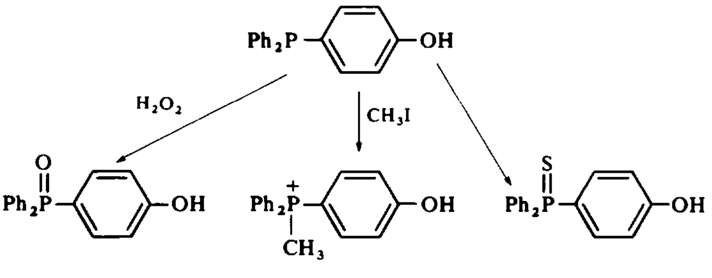
Ionization constants for phosphorus-substituted phenols. Since the electron-acceptor properties of substituents in the benzene ring are most prominent in the electron-donating reaction centre, we determined the ionization constants for several *para*-phosphorus-substituted phenols and calculated the nucleophilic σ^--constants for the corresponding substituents.[36]

TABLE 5. M.PS OF PHOSPHORUS-SUBSTITUTED PHENOLS p-RC_6H_4OH

Substituent R	M.P., [a] °C	M.P., °C (Published data)
Ph_2P	114–115 (benzene–petr.ether)	113–114[37] 105–106[38]
$Ph_2P(O)$	250–251 (MeOH)	243–244[37] 244–246[38] 241·5–242·5[18]
$Ph_2P(S)$	176·5–177·5 (benzene)	—
Ph_2MeP^+ J^-	182·5–183·5 (i-PrOH)	—

[a] Corrected values.

p-Diphenylphosphinophenol was obtained by the method of Senear *et al.*[37] Its derivatives were synthesized[36] according to the following scheme (the constants are given in Table 5)



The ionization constants for phosphorus-containing phenols in aqueous alcohols (1:1 v/v) are listed in Table 6. The ionization constants for a number of *para*- or *meta*-substituted phenols with known σ^-- and σ-constants were determined in the same solvent (Table 7). On the basis of these data we derived the correlation equation which was used for the calculation of σ^--constants for phosphorus-containing groups

TABLE 6. IONIZATION CONSTANTS (pK_a) FOR *p*-SUBSTITUTED PHENOLS $p\text{-}RC_6H_4OH$ IN AQUEOUS ALCOHOL (1:1 v/v, 25°) AND THE CORRESPONDING σ^-- AND σ-CONSTANTS FOR THE SUBSTITUENTS R

NN	R	pK_a	σ^-	σ^- Published data	σ	$\sigma^- - \sigma$	σ^-_R
1.	Ph_2P	10·46	0·26	0·32[25, 26]	0·19	0·07	0·16
2.	$Ph_2P(O)$	9·38[a]	0·68	0·88[25, 26]; 0·680[18] 0·845[28]	0·53	0·15	0·35
3.	$Ph_2P(S)$	9·49	0·63	0·73[25, 26]	0·47	0·16	0·44
4.	$Ph_2CH_3\overset{+}{P}$	7·82	1·28	1·09[25, 26]	—	—	—

[a] Published data[18]: pK_a = 9·48.

TABLE 7. IONIZATION CONSTANTS (pK_a) FOR SUBSTITUTED PHENOLS RC_6H_4OH IN AQUEOUS (1:1 v/v, 25°) AND THE CORRESPONDING σ^- (OR σ) CONSTANTS FOR THE SUBSTITUENTS R

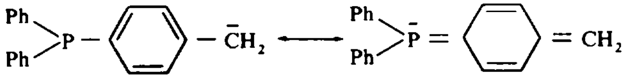
R	*p*-CH_3	*p*-CH_3O	H	*p*-Br	*p*-I	*p*-COOMe	*m*-NO_2	Ac	*p*-NO_2	Equations
pK_a	11·46	11·41	11·21	10·47	10·42	9·49	9·25	9·08	7·87	$\lg K_a = -11{\cdot}12 + 2{\cdot}569\cdot\sigma^- \pm 0{\cdot}07$
pK_a (published data)	11·60[39]	11·50[39] 11·72[18]	11·16[39] 11·47[18]	10·57[39] 10·60[18]	— —	— —	9·25[40] 9·35[18]	9·06[39]	7·89[39] 7·95[18]	$\sigma = 4{\cdot}32 + 0{\cdot}383\cdot\lg K_a \pm 0{\cdot}04$ r 0·998
σ^- (or σ)	−0·15[39]	−0·13[39]	0	0·25[39]	0·276[41]	0·64[a]	0·71[23]	0·84[39]	1·24[39]	

[a] σ^--value for *p*-COOEt[39] was used.

(Table 7). These σ^--constants are listed in Table 6; in the same Table we gave for comparison the corresponding σ-constants, $\sigma^- - \sigma$- and σ_R^--values together with σ^--constants obtained by Schiemenz from half-neutralization potentials for phosphorus-substituted dimethyl anilines.[25, 26] Our data differ slightly from the results obtained by Schiemenz and also from those by Bott, *et al.*,[28] who studied alkaline decomposition kinetics for phosphorus-substituted trimethylbenzylsilanes. The difference is probably due to the difference in the reaction series. For one of the reaction series our results for the $Ph_2P(O)$ group coincide with the value reported by Monagle, *et al.*[18]

It appears that the σ^--constants for phosphorus-containing substituents are positive and are higher than the corresponding σ-constants, and this indicates the effect of direct polar conjugation with the reaction centre. In the case of Ph_2P group, the difference $\sigma^- - \sigma$ for phenols is 0·07 and for substituted dimethylanilines it is 0·13 according to the data by Schiemenz. Therefore, the electron-acceptor effect of direct polar conjugation of trivalent phosphorus with the electron-donating reaction centre although weak is clearly revealed.

Protophilic deuteroexchange of certain deuterated arylphosphines. We have studied* protophilic hydrogen exchange kinetics for several deuterated arylphosphines.[42–44] The electron-acceptor effect of the Ph_2P group is evident from the rates of exchange in deuterated Me groups of diphenyl-*m*- or *p*-tolyphosphines. The exchange in the *para*-Me group appeared to proceed 25 times as fast as that in the *meta*-Me group (t.-BuOH-diglime, t.-BuOK, 120°). These data indicate the conjugation in a transition state arising during the exchange and probably possessing the carbanion structure.



The Ph_2N group as opposed to the Ph_2P group decreases[42] the exchange rate in the *para*-Me group compared with that in the *meta*-position which agrees with its + *M*- and − *I*-effects. The partial rate factors for the exchange at *ortho*-, *meta*- or *para*-positions of triphenylphosphine and triphenylamine also revealed the essential differences between nitrogen and phosphorus electron effects.

p-π-*Conjugation and hybridization of a lone pair of electrons.* The above arguments support the conclusion that the Ph_2P and other groups containing trivalent phosphorus must be regarded as second-kind substituents. As mentioned, the electron-acceptor properties of trivalent phosphorus may be accounted for by p_π-d_π-conjugation and either the absence or negligibility of oppositely directed *p*-π-interaction.

The first effect was repeatedly discussed in the literature[45] and applied to explain the properties of P^{III}-compounds. In particular, the experimental support for the d-orbital resonance is provided by the ease of metallation of methyl[46] or benzyl groups[47] bonded to trivalent phosphorus and also by high isotope exchange rates in P-Me groups compared with those in N-Me groups. Not only intra- but also some intermolecular interactions seem to be caused by the vacant d-orbitals. For example, triphenylphosphine in contrast with triphenylamine forms the complex compound

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* Together with E. Yakovleva and A. Shatenshtein.

with hexamethylbenzene[48] and exchanges a phenyl radical for a tolyl radical under the action of *p*-tolyllithium[49] forming probably an intermediate compound $[Ph_3PC_6H_4CH_3{-}p]^-Li^+$. However, the *d*-orbital conjugation effect alone cannot completely account for the *meta*-orienting effect of trivalent phosphorus since p_π–d_π-conjugation takes place also with sulphur and chlorine which are, nevertheless, *ortho–para*-orientating.

The absent or negligibly weak effect of *p*-π-conjugation which we stipulated in discussing the reasons for β-orientation of piperidine addition to vinyl-P^{III} compounds has been confirmed by various chemical methods. Our data also provides a means of estimating the *p*-π-conjugation strength. The difference in σ_R-values for Ph_2P and $Ph_2P(O)$ groups on the one hand from the increase in p_π–d_π-conjugation on account of positive charge at the tetra-coordinated phosphorus atom and the contracted *d*-orbitals, and, on the other hand, from the absence of *p*-π-conjugation which may possibly be present in the case of trivalent phosphorus. We could not evaluate the contributions made by each of these effects, but the total contribution, i.e. the difference between σ_R-values for these groups is as small as 0·12, which indicates the *p*-π-conjugation effect to be probably zero. This is confirmed by physical data, e.g. NMR-F^{19} study of phosphorus-substituted fluorobenzenes reported by Taft and Rakshys[33] shows that phosphorus has the weakest π-donor effect of all the period III elements. The opposite signs of dipole moments for aromatic phosphines or amines are also indicative of the weak tendency of phosphorus to *p*-π-conjugations: in the first case the negative pole of a dipole is phosphorus, in the second—the phenyl centre.[50] Therefore, the qualitative order of mesomeric effects of the third period elements should be as follows:

$$RS \approx Cl \gg R_2P$$

Perhaps this rearrangement is due to the weaker overlap of 3*p*-2*p*-orbitals as compared with that of 2*p*-2*p*-orbitals. This must then be valid for all the elements of the period III. But phosphorus shows a sharp fall of *p*-π-conjugation as compared with sulphur and chlorine, which cannot be accounted for on this basis alone.

To account for the "abnormal" properties of a lone pair of electrons in phosphorus, two of the authors together with Bochvar[11,51] proposed that the weak tendency of trivalent phosphorus to *p*-π-conjugation is caused by the hybridization of the orbital of a lone electron pair. A lone pair of electrons is known to involve a certain amount of *p*-character when forming a π-bond; the electrons in the *s*-state are incapable of conjugation since the overlap integral between *s*- and p_z-orbitals is zero.[52] Therefore, *p*-π-conjugation becomes stronger the greater the amount of *p*-state involved in the hybridization of a lone pair electrons.

The relation between hybridization and participation of the lone pairs in conjugation should definitely be revealed by the elements of group V possessing in the trivalent state a single lone pair of electrons which may be an unhybridized *s*-pair in some cases.

In order to estimate approximately the hybridization of a lone pair, one may apply the relationship between the hybridization of atomic orbitals and the valence angles at a heteroatom in a molecule.[52] We have to assume that σ-bonds are formed only by *s*-*p*-hybrid orbits and that they are not bending bonds. The contribution of *d*-orbitals to the formation of σ-bonds is generally thought to be small and negligible.* d-Orbitals are, however, responsible for π-bonding of substituents to phosphorus. Such an approach is used in a number of investigations of P^{III} and P^{V} compounds.[53–61]

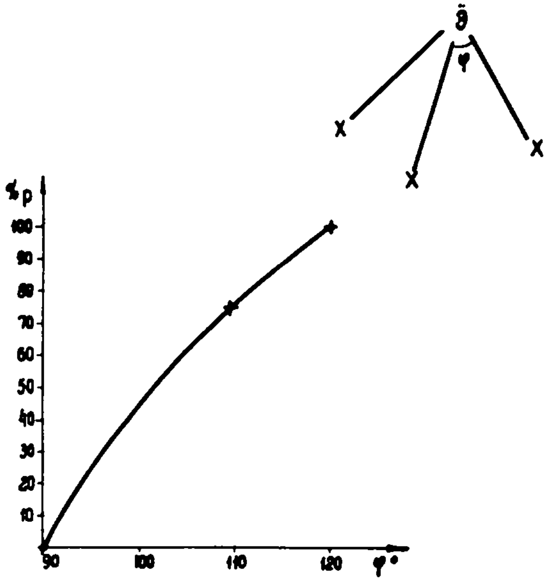

FIG. 1 p-Character on a lone pair of electrons as a function of the valence angle.

Fig. 1. gives the p-character of an orbital occupied by a lone pair of phosphorus electrons or by that or another element E as a function of the valence angle X–E–X in a pyramidal molecule EX_3.

The analytical expression for this function was obtained[51] by applying the orthogonality condition to the hybrid atomic orbitals:

$$\%P = \frac{3\cos\varphi}{\cos\varphi\text{-}1}\cdot 100\%$$

This relationship accounts for the weak tendency of the lone pair of phosphorus electrons to p-π-conjugation. Indeed, the space geometry of phosphorus compounds of the type PX_3[65] (X = Hal, Alk, Ar, OAlk) gives the valence X–P–X angle to be about 100°.[65, 66] This angle remains constant in various cyclic compounds (for instance, in cyclopolyphosphines, phosphorus anhydride). In phosphine and tricyanophosphine the valence angles are nearly 90°, in primary and secondary phosphines they gradually increase approaching 100°. The angles at the P atom vary little even in the case of substituents able to conjugate with a lone pair of electrons. Thus C–P–C-angles are very close for triphenyl- and trimethyl phosphine. The same is true of tricyano- and trisilylphosphines[67] whose valence angles are close to those for phosphine.

The valence angles in analogous nitrogen compounds are generally larger and are nearly tetrahedral in ammonia and alkylamines.[68–77] The substituents capable of

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* Some authors believe that d-orbitals participate in the formation of hybrid σ-bonds.[62–64].

p-π-conjugation produce sharp changes in nitrogen valence angles as opposed to phosphorus. For example, phenyl, nitro-or-carbonyl groups increase the valence angle by approximately 10 degrees making it almost 120° in some cases.

Using the diagram, Fig. 1, one can estimate the hybridization character for the lone pair in these compounds. Generally the amount of *p*-character of a lone pair of electrons is 40–50% which corresponds to the valence angle 100 ± 1°. This amount is further lowered for secondary and especially for primary phosphines. The phosphine lone pair is an almost unhybridized s-pair. Lone pairs of tricyan- and trisilylphosphines have also an almost complete *s*-character.

Lone pairs of nitrogen compounds with similar structure involve a higher degree of *p*-character (70% and more) becoming almost pure *p*-pairs when substituents capable of *p*-π-conjugating are involved. It then clarifies the origin of the different electron influence of diphenylphosphino and diphenylamino groups upon the benzoic acids ionization constants and isotope exchange rate for the corresponding tolyl substituted derivatives. A still sharper difference in hybridization (10–20% of *p*-character against 90%) is observed for cyano and silicon substituents bonded to phosphorus or nitrogen. In these compounds phosphorus lone pairs seem to be incapable of *p*-π-conjugation.

The phosphorus pyramidal configuration is fairly stable as indicated by the high activation energy for the racemization of optically active phosphines (about 30 kcal/mole for (+)-methylpropylphenyl phosphine[78]). The increase in amount of *p*-character of a lone pair and hence the change in valence angles requires energy which is not compensated by *p*-π-conjugation energy because the latter even in most favourable cases (conjugation of amino group with the phenyl ring) does not exceed 10 kcal/mole[79] being considerably lower for the phosphino group. It now becomes clear why phosphorus valence angles do not increase even if substituents capable of conjugating with a lone pair of electrons are involved. The above relationship between the phosphines optical activity and a weak tendency of phosphorus lone pair to *p*-π-conjugation is evidently typical not only of phosphorus. The absence of *p*-π-conjugation (or its negligibility) should be expected for those types of compounds whose asymmetrical molecules can exist in optically active form in spite of the central asymmetric atom possessing a lone pair of electrons. This criterion may be applied to the study of *p*-π-conjugation when the data on molecular geometry are not available. From this viewpoint the weak tendency to *p*-π-conjugation due to the enhanced *s*-character of a lone pair of electrons must be expected for the compounds of arsenic, antimony, bismuth, for sulphonium salts or sulphoxides. The diminished tendency to conjugation was observed also for certain amines with "abnormal" valence angles.*

Based on an idea of low *p*-contribution of the lone pair of phosphorus electrons one may possibly explain a number of peculiar properties of P^{III} compounds.

For instance, the lack of aromatic properties shown by phosphols[82] may possibly be due to the enhanced *s*-character on the lone pair of phosphorus electrons.[51] A similar explanation was suggested by Schindlbauer[83] on the basis of UV spectral analysis and the data on dipole moments for isomeric tri(tolyl)phosphines. The hybridization of a lone pair of an element, of course, exerts a strong influence upon its

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* Several examples of this kind are reported.[80, 81]

basicity, nucleophilicity, dipole moments and spectral parameters of the compounds. This has been discussed by many authors.[80, 84–87] A number of peculiar chemical and physical properties observed for acyl phosphides[88–90] may probably also be accounted for by the enhanced *s*-character on the lone pair of electrons.

Finally, our results on the orientating effect of trivalent phosphorus and the results obtained by other authors are inconsistent with the conclusions recently published by the SCF method.[91] These calculations require that phenylphosphine, diphenylphosphine and triphenylphosphine form the following series according to the electron density distribution in the ring: *ortho* > *para* > *meta*. Therefore the calculations require trivalent phosphorus not to be different from the *ortho–para*-orientating groups if the effect on the electron density distribution in the benzene ring is considered. However, this is inconsistent with the existing chemical data.

REFERENCES

[1] W. Pritzkov, *Theoretische Gesichtspunkte in der organishen Chemie*, p. 49. Dresden and Leipzig (1963); T. I. Temnikova, *Kurs teoreticheskih osnov organicheskoi khimii, Izd-vo "Khimia"* 150 (1968).

[2] A. N. Pudovik, *Uspekhi khimii* **23**, 575 (1954).

[3] M. I. Kabachnik, E. N. Tsvetkov and Chang Chun-Yu, *Zh. Obshch. Khim.* **32**, 3340 (1962).

[4] M. I. Kabachnik, T. Y. Medved', Y. M. Polikarpov and K. C. Yudina, *Izv. Akad. Nauk. SSSR, OKhN* 1584 (1962).

[5] M. I. Kabachnik, E. N. Tsvetkov and Chang Chun-Yu, *Tetrahedron Letters* 5 (1962).

[6] D. Seyferth, *Progr. Inorg. Chem.* **3**, 137 (1962).

[7] N. S. Nametkin, V. N. Perchenko, I. A. Grushevenko and G. L. Kamneva, *Izv. Akad. Nauk, SSSR, Ser. Khim.* 2074 (1968).

[8] D. J. Peterson, *J. Org. Chem.* **31**, 950 (1966).

[9] W. E. Parham and R. F. Motter, *J. Am. Chem. Soc.* **81**, 2146 (1959).

[10] E. M. Popov, E. N. Tsvetkov, Chang Chun-Yu and T. Y. Medved', *Zh. Obshch. Khim.* **32**, 3255 (1962).

[11] E. N. Tsvetkov, D. I. Lobanov and M. I. Kabachnik, *Teor. i Eksper. Khim.* **1**, 729 (1965).

[12] E. N. Tsvetkov, D. I. Lobanov and M. I. Kabachnik, *Ibid.* **2**, 458 (1966).

[13] H. Gilman and G. E. Brown, *J. Am. Chem. Soc.* **67**, 824 (1945).

[14] H. Schindlbauer, *Monatsh, Chem.* **96**, 1021 (1065).

[15] G. P. Schiemenz, *Chem. Ber.* **99**, 504 (1966).

[16] R. A. Baldwin, M. T. Cheng and G. D. Homer, *J. Org. Chem.* **32**, 2176 (1967).

[17] H. Gilman and G. E. Brown, *J. Am. Chem. Soc.* **62**, 3208 (1940).

[18] J. J. Monagle, J. V. Mengenhauser and D. A. Jones Jr., *J. Org. Chem.* **32**, 2477 (1967).

[19] W. L. Bright and H. T. Briscoe, *J. Phys. Chem.* **37**, 787 (1933).

[20] J. D. Roberts, E. A. McElhill and R. Armstrong, *J. Am. Chem. Soc.* **71**, 2923 (1949).

[21] J. D. Roberts and C. M. Reagan, *Ibid.* **75**, 4102 (1953).

[22] J. P. Schaefer and T. J. Miraglia, *Ibid.* **86**, 64 (1964).

[23] D. H. McDaniel and H. C. Brown, *J. Org. Chem.* **23**, 420 (1958).

[24] J. L. Roberts and H. H. Jaffe, *J. Am. Chem. Soc.* **81**, 1635 (1959).

[25] G. P. Schiemenz, *Angew. Chem.* **78**, 145 (1966); *Ibid.* Internat. Edit. **5**, 129 (1966).

[26] G. P. Schiemenz, *Ibid.* **78**, 605 (1966); *Ibid.* internat. Edit. **5**, 595 (1966).

[27] R. Rabinowitz, R. Markus and J. Pellon, *J. Polymer Sci.* A, **2**, 1241 (1964).

[28] R. W. Bott, B. F. Dowden and C. Eaborn, *J. Chem. Soc.* 4994 (1965).

[29] B. I. Stepanov, A. I. Bokanov and B. A. Korolev, *Zh. Obshch. Khim.* **37**, 2139 (1967).

[30] G. P. Schiemenz, *Angew. Chem.* **78**, 777 (1966); *Ibid.* Internat. Edit. **5**, 731 (1966).

[31] H. L. Retcofsky and C. E. Griffin, *Tetrahedron Letters* 1975 (1966).

[32] H. Schindlbauer, *Chem. Ber.* **100**, 3432 (1967).

[33] R. W. Taft and J. W. Rakshys Jr., *J. Am. Chem. Soc.* **87**, 4387 (1965).

[34] J. W. Rakshys, R. W. Taft and W. A. Sheppard, *Ibid.* **90**, 5236 (1968).

[35] A. W. Johnson and H. L. Jones, *Ibid.* **90**, 5232 (1968).

[36] E. N. Tsvetkov, M. M. Makhamatkhanov and M. I. Kabachnik, *Teor. i Eksper. Khim.* **3**, 824 (1967).

[37] E. A. Senear, W. Valient and J. Wirth, *J. Org. Chem.* **25**, 2001 (1960).

[38] O. Neunhoeffer and L. Lamza, *Chem. Ber.* **94**, 2519 (1961).

[39] L. A. Cohen and W. M. Jones, *J. Am. Chem. Soc.* **85**, 3397 (1963).

[40] J. Schwartzenbach and E. Rudin, *Helv. Chim. Acta* **22**, 360 (1939).

[41] H. Jaffe, *Chem. Revs.* **53**, 191 (1953).

[42] E. A. Yakovleva, E. N. Tsvetkov, D. I. Lobanov, M. I. Kabachnik and A. I. Shatenshtein, *Tetrahedron Letters* No 35, 4161 (1961): *Dokl. Akad. Nauk SSSR* **170**, 1103 (1966).

[43] E. A. Yakovleva, E. N. Tsvetkov, D. I. Lobanov, M. I. Arshinova, A. I. Shatenshtein and M. I. Kabachnik, *Izv. Akad. Nauk SSSR, Ser. Khim.* 2012 (1968).

[44] E. A. Yakovleva, E. N. Tsvetkov, D. I. Lobanov, A. I. Shatenshtein and M. I. Kabachnik, *Tetrahedron* **25**, 1165 (1969).

[45] R. F. Hudson, *Structure and Mechanism in Organo-Phosphorus Chemistry*. London (1965).

[46] D. J. Peterson and H. R. Hays, *J. Org. Chem.* **30**, 1939 (1965); D. J. Peterson and J. H. Collins, *Ibid.* **31**, 2373 (1966); D. J. Peterson, *J. Organometal. Chem.* **8**, 199 (1967); L. Horner, W. D. Balzer and D. J. Peterson, *Tetrahedron Letters* 3315 (1966).

[47] A. M. Aguiar, J. Giacin and A. Mills, *J. Org. Chem.* **27**, 674 (1962); A. M. Aguiar, J. Beisler and A. Mills, *Ibid.* **27**, 1001 (1962).

[48] R. A. Shaw, B. C. Smith and C. P. Thakur, *Chem. Commun*, 228 (1966).

[49] G. Wittig and A. Maercker, *J. Organometal. Chem.* **8**, 491 (1967).

[50] G. Klages and R. Langpape, Z. Elektrochim. *Ber. Bunsenges phisik. Chem.* **63**, 533 (1959); H. Schindlbauer, G. Hajek, *Chem. Ber.* **96**, 2601 (1963).

[51] E. N. Tsvetkov, D. A. Bochvar and M. I. Kabachnik, *Teor. i Eksper. Khim.* **3**, 3 (1967).

[52] C. A. Coulson, *Valence*. Oxford (1961).

[53] N. Muller, P. C. Lauterbur and J. Goldenson, *J. Am. Chem. Soc.*, **78**, 3557 (1956).

[54] J. R. Parks, *Ibid.* **79**, 757 (1957).

[55] D. Purdela, *Rev. Roumaine Chim.* **10**, 925 (1965).

[56] H. S. Gutowsky and J. Larmann, *J. Am. Chem. Soc.* **87**, 3815 (1965).

[57] J. H. Letcher and J. R. Van Waser, *J. Chem. Phys.* **44**, 815 (1966).

[58] P. Kisliuk, *Ibid.* **22**, 86 (1954).

[59] K. Issleib and W. Grundler, *Theoret. chim. Acta Berl.* **6**, 64 (1966); **8**, 70 (1967).

[60] P. C. Van Der Voorn and R. S. Drago, *J. Am. Chem. Soc.* **88**, 3255 (1966).

[61] K. E. Banyard and R. B. Hake, *J. Chem. Phys.* **43**, 2684 (1965).

[62] R. S. Mulliken, *J. Am. Chem. Soc.* **77**, 887 (1955).

[63] G. S. Blevins, A. W. Jache and W. Gordy, *Phys. Rev.* **97**, 684 (1955); A. W. Jache, G. S. Blevins and W. Gordy, *Ibid.* **97**, 680 (1955); C. A. Burrus and W. Gordy, *Ibid.* **92**, 274 (1953).

[64] D. B. Boyd and W. N. Lipscomb, *J. Chem. Phys.* **46**, 910 (1967).

[65] D. E. C. Corbridge, *Topics in Phosphorus Chemistry* Vol **3**, p. 57 (1966).

[66] L. V. Vilkov, P. A. Akishin and G. E. Salova, *J. Strukt. Khim.* **6**, 355 (1965).

[67] B. Beagley, *Chem. Commun.* 601 (1967).

[68] M. T. Weiss and M. W. P. Strandberg, *Phys. Rev.* **83**, 567 (1951).

[69] T. Nishikawa, T. Itoh and K. Shimoda, *J. Chem. Phys.* **23**, 1735 (1955).

[70] S. H. Bauer, *J. Am. Chem. Soc.* **60**, 524 (1938).

[71] D. R. Lide Jr and D. E. Mann, *J. Chem. Phys.* **28**, 572 (1958).

[72] Y. Sasaki, K. Kimura and M. Kubo, *Ibid.* **31**, 477 (1959).

[73] C. C. Costain and J. M. Dowling, *Ibid.* **32**, 158 (1960).

[74] J. K. Tyler, *J. Molec. Spectrosc.* **11**, 38 (1963).

[75] L. V. Vilkov and T. P. Timasheva, *Dokl. Akad. Nauk SSSR* **161**, 351 (1965).

[76] D. G. Lister and J. K. Tyler, *Chem. Commun*, 152 (1966).

[77] K. Hedberg, *J. Am. Chem. Soc.* **77**, 6491 (1955).

[78] L. Horner and H. Winkler, *Tetrahedron Letters* 461 (1964).

[79] B. Pullman and A. Pullman, *Les theories electroniques de la chemie organique* p. 240. Paris (1952).

[80] A. T. Bottini and C. P. Nach, *J. Am. Chem. Soc.* **84**, 734 (1962).

[81] V. F. Bystrov, O. A. Yuzhakova and R. G. Kostyanovskij, *Dokl. Akad. Nauk SSSR* **147**, 843 (1962); R. G. Kostyanovsky, O. A. Yuzhakova and V. F. Bystrov, *Zh. Vsesoyusn. Khim. Obshch. im. Mendeleeva* **10**, 229 (1965).

[82] E. H. Braye, W. Hubel and J. Caplier, *J. Am. Chem. Soc.* **83**, 4406 (1961); G. M. Campbell, R. C. Cookson, M. B. Hocking and A. N. Hughes, *J. Chem. Soc.* 2184 (1965).

[83] H. Schindlbauer, *Monatsch. Chem.* **96**, 1794 (1965).

[84] J. H. Gibbs, *J. Chem. Phys.* **22**, 1460 (1954); W. A. Henderson Jr and C. A. Streuli, *J. Am. Chem. Soc.* **82**, 5791 (1960); K. Issleib and H. Bruchlos, *Z. anorg. allgem. Chem.* **316**, 1 (1962).

[85] W. A. Henderson Jr and S. A. Buckler, *J. Am. Chem. Soc.* **82**, 5794 (1960); V. Mark and J. K. Van Waser, *J. Org. Chem.* **29**, 1006 (1964).

[86] R. F. Hudson, *Pure and Appl. Chem.* **2**, 371 (1964).

[87] J. R. Weaver and R. W. Parry, *Inorg. Chem.* **5**, 718 (1966).

[88] R. Tyka and E. Plazek, *Bull. Acad. Polon. Sci., Ser. Chem.* **9**, 577 (1961); *Roczniki Chem.* **35**, 183 (1961).

[89] K. Issleib and O. Low, *Z. anorg. allgem. Chem.* **346**, 241 (1966).

[90] R. G. Kostyanovsky, V. V. Yakshin and S. L. Zimont, *Tetrahedron* **24**, 2995 (1968).

[91] B. R. Russell, R. M. Hedges and W. R. Carper, *Molec. Phys.* **12**, 283 (1967); M. Jaro, P. Knowlton, J. E. Bissey, H. Goldwhite and W. R. Carper, *Ibid.* **13**, 165 (1967).