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THE INVESTIGATION OF THE ELECTRONIC STRUCTURE OF POLYFLUOROAROMATIC PHOSPHINES BY MEANS OF X-RAY FLUORESCENT AND ULTRAVIOLET (He I) PHOTOELECTRON SPECTROSCOPY

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SUMMARY

The electronic structure of polyfluoroaromatic phosphines of $C_6F_5PX_2$ type (X = H, CH_3, C_6H_5, C_6F_5, F, Cl, OCH_3, NCS, $N(C_2H_5)_2$) together with those of their hydrocarbon analogues and model compounds of PX_3 type (X = H, C_2H_5, Cl, OCH_3, NCS, $N(C_2H_5)_2$) has been investigated by photoelectron (He I) and X-ray fluorescent spectroscopy methods. The spectral data obtained have been interpreted on the basis of MINDO/3 calculations being in good agreement with the experimental results. A new scheme for orbital interaction in aromatic and polyfluoroaromatic phosphines has been elaborated using MINDO/3 calculation data together with X-ray fluorescent PK_β-spectra of investigated compounds. The existence of a relatively effective p_Π-p_Π interaction between the phosphorus atom and the Π-system of the aromatic ring and the decrease of

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the effectiveness of the latter in polyfluoroaromatic phosphines in respect to their hydrocarbon analogues have been proved. The same effect has been shown to take place also in corresponding polyfluoroaromatic derivatives of nitrogen, oxygen, and sulfur. The charges on phosphorus atoms in the investigated phosphines have been determined from X-ray fluorescent PKα-shifts. The connection between the electronic structure and the reactivity of polyfluoroaromatic phosphines in reactions occuring on the phosphorus atom as a reaction center has been discussed.

INTRODUCTION

The chemical behavior of organic phosphines is substantially determined by their Π-donor properties connected with low-energy frontier electron density. The most important reactions permitting interpretation in these terms are, e.g., protonation [1-3] (cf. [4-5]) and the formation of complexes [6]. The influence of substituents at phosphorus on the reactivity of phosphines in such reactions can be described on the basis of changes in characteristics of higher occupied MO's of phosphines, especially of the frontier occupied MO (HOMO), depending on the nature of substituents.

HOMO in aromatic phosphines is known to be a Π-MO,mainly localized on the phosphorus atom [7,8], and so its characteristics (energy and localization) must be determined mainly by Π-interaction between phosphorus and substituents bonded with the latter. Such interaction has been shown to occur by a complex mechanism involving both p_{Π}-p_{Π}- and d_{Π}-p_{Π}-conjugation effects [9], but the relative role of them is known to be the object of discussion. Thus, there are arguments in the literature both for the existance of p_{Π}-p_{Π}-conjugation of phosphorus lone electron pair (LEP) with substituents [7-14] and for the absence of this type of conjugation or its negligible effectiveness [15-21]. The situation with d_{Π}-p_{Π}-conjugation is also controversial (see, e.g., [22,23]).

Earlier we have shown that the substitution of aryl radicals on the heteroatom by polyfluroaryl ones in the aromatic sulfides substantially diminishes the effectiveness of conjugation of sulfur LEP with the aromatic Π-system [24,25]. That effect leads to significant changes in energy and localization of HOMO and hence in reactivity of these compounds. It was of interest to investigate the effects induced by introduction of pentafluorophenyl groups in the molecules of aromatic phosphines where the conditions for the conjugation of heteroatom LEP (and the nature of the latter) substantially differ from those in corresponding sulfides.

In our previous work on the relationship between the electronic structure and reactivity of (arylethynyl)arylphosphines, the presence of a pentafluorophenyl group at the phosphorus atom has been shown to change the stucture and the energy of higher occupied MO's of phosphines, leading to their lower reactivity towards tetracyanoethylene (TCNE) [26]. It seemed appropriate to study the nature of that effect on a wider range of examples.

Thus, the problems to solve in the present work included the investigation of the changes in characteristics of higher occupied MO's in polyfluoroaromatic phosphines under the influence of pentafluorophenyl groups and the connection between the observed variations in electronic structure of these compounds and in their reactivity in cases when the latter can be interpreted in terms of frontier orbital approach [27].

RESULTS AND DISCUSSION

The electronic structure of phosphines has been investigated in the present work by means of phosphorus X-ray fluorescent K_α- and K_β-spectra permitting us to determine the charges on phosphorus, together with the relative one-electron energies of occupied MO's containing the contribution of 3p(P)-AO's and to estimate qualitatively the degree of that contribution [28-30]. We have also obtained the vertical ionization potentials (IP) of a number of the polyfluoroaromatic phosphines being studied by He I ultraviolet photoelectron (UPE) spectroscopy. The former in approximation of Koopman's theorem [31] correspond (with the opposite sign) to the absolute one-electron energies of occupied MO's. The UPE spectra of aromatic phosphines it should be noted have been recorded in only few works [32-39], and their interpretation has often been unsatisfactory or, at least, contradictory. Our interpretation has been based on X-ray fluorescent data together with quantum-chemical calculations by the MINDO/3 method in s,p-basis [40]. The latter have been used successfully in the previous studies of the electronic structure of aromatic phosphines [41].

Polyfluoroaromatic phosphines of the $C_6F_5PX_2$ type (I) [X = H a, CH_3 b, C_6H_5 c, C_6F_5 d, F e, Cl f, OCH_3 g, NCS h, $N(C_2H_5)_2$ i] with a number of hydrocarbon analogues $C_6H_5PX_2$ (II) [X = H a, CH_3 b, C_6H_5 c, F e, Cl f, $N(C_2H_5)_2$ i] and trisubstituted phosphines PX_3 (III) [X = H a, CH_3 b, F e, Cl f, OCH_3 g, NCS h, $N(C_2H_5)_2$ i, C_2H_5 j, OC_6H_5 k, OC_6F_5 l] have been chosen as compounds for investigation in present work. These phosphines have been synthesized according to known literature methods (see also [3]).

In Fig. 1 the PK_β-spectra of phosphines containing, at phosphorus atoms, hydrogen, alkyl, aryl and polyfluoroaryl groups have been shown. The positions of maxima in the PK_β -spectra have been listed in Table 1 in comparison with the data from the PES method (where possible). The good agreement between the relative values of IP's (from PES data) and the relative energies of corresponding X-ray transitions (considered as maxima in K_β spectra) should be noted (Table 1; cf. also Table 6). The latter has been used in the present work for the assignment of UPE spectra on the basis of contributions of heteroatom AO's (determined by the X-ray fluorescent method) in MO's with known relative energies.

The short-wave maximum A in the PK_β-spectrum of (IIIa) is known to be assigned to the phosphorus LEP (its 3p-component) and maximum C to P-H σ-bond levels [43]. A similar assignment can be made for the PK_β-spectrum of (IIIk) (Fig.1).

The introduction of the aryl group into the molecule of (IIIa) leads to considerable changes in the PK_β-spectrum (Fig. 1). Thus, the short-wave region of the PK_β-spectra of compounds (Ia) and (IIa) contains three well-resolved maxima A', A'' and B, the former lying in the shorter wave region relative to the initial maximum A in the PK_β-spectrum of (IIIa). That fact indicates the redistribution of 3p(P)-electron density by a number of MO's as a result of p_π-p_π-interaction of phosphorus LEP with the π-system of the aryl substituent.

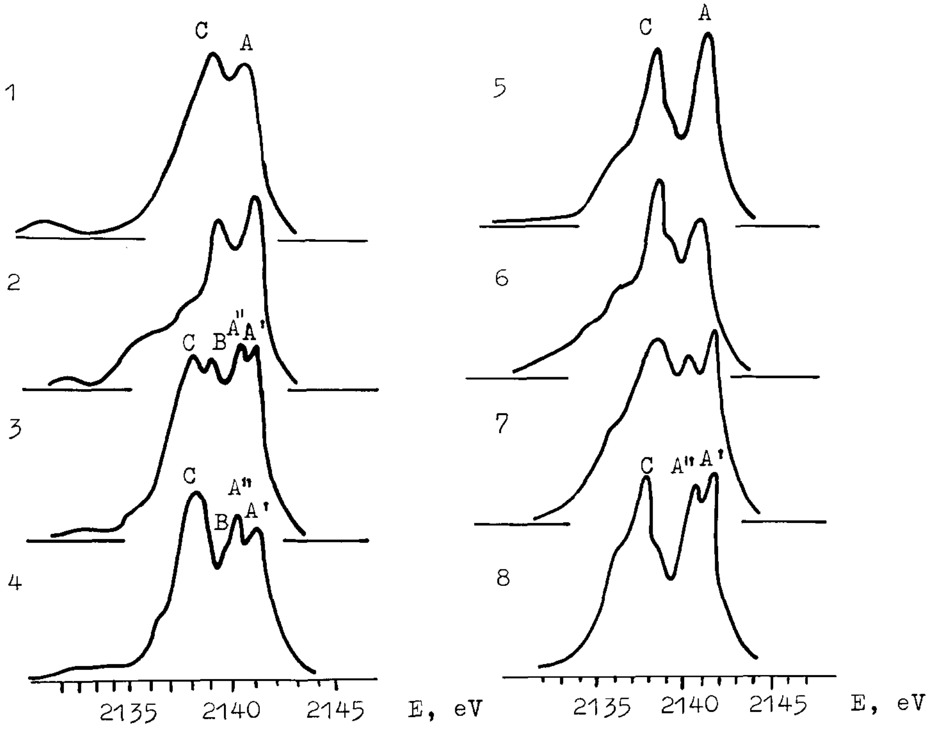

Fig.1. PK_β -spectra of arylphosphines and model compounds :
1. PH_3 (IIIa); 2. $P(C_2H_5)_3$ (IIIj); 3. $C_6H_5PH_2$ (IIa);
4. $C_6F_5PH_2$ (Ia); 5. $C_6F_5P(CH_3)_2$ (Ib); 6. $P(C_6H_5)_3$ (IIc);
7. $C_6F_5P(C_6H_5)_2$ (Ic); 8. $P(C_6F_5)_3$ (Id)

The existence of such redistribution follows also from MINDO/3 calculation data (Table 2). On Fig. 2 the experimental and theoretical (on the basis of calculations by that method) PK_β-spectra of the aromatic (IIa), (IIc) and polyfluoroaromatic (Ia), (Ib) phosphines have been shown. The representation of these spectra with a common energy scale has been made by the first IP value. The comparison of the spectra of Fig. 2 demonstrates clearly the good reproduceability of the experimental PK_β-spectra (and hence the MO structure of the investigated phosphines) by the MINDO/3 calculation data. A good agreement between the values of IP's obtained for the compounds (Ia), (Ib), (IIa), (IIb), (IIc) by PES method and those calculated by MINDO/3 method follows from the Table 2.

The analysis of PK_β-spectra together with MINDO/3 calculation data allow us to conclude that the known scheme of level splitting due to the interaction of the heteroatom LEP with the aromatic Π-system [25,45] used recently for the assignment of PES spectra of aromatic phosphines [39] does not explain the presence of three maxima in the short-wave region of the PK_β-spectra of (Ia) and IIa) (Fig. 1,2 ; cf. Tables 1 and 2). According to X-ray fluorescent and MINDO/3 calculation data the interaction of the phosphorus LEP with the Π-system of aryl and polyfluoroaryl substituent is more complicated because of the substantial mixing of the orbitals of the σ- and Π-type which cannot be neglected. The latter is due to the non-planarity of the molecules of phosphines.

The presence of three maxima corresponding to a 3p(P)-AO contribution to higher occupied MO's in the PK_β-spectrum of (Ia) and (IIa) can be explained as follows (Fig. 3). The initial interaction of degenerated $1e_{1g}$-orbital of the benzene ring with phosphorus LEP gives, as in the case of other heteroatoms [25,45], three MO's corresponding to (b_1-n_p)-, a_2- and (b_1+n_p)-orbitals of Π-type. Furthermore, the orbitals (b_1-n_p)- and (b_1+n_p) - because of non-planarity of the molecule can interact with a low-energy orbital of the σ-type localized mainly on P-H and P-C bonds. The ionization potential corresponding to such an orbital is relatively high (12.4 eV for CH_3PH_2 [46])

TABLE 1

Vertical ionization potentials and the energies of corresponding X-ray transitions in PKβ-spectra of investigated phosphines.

Compound	IP's (from PES data), eV		The corresponding maxima in PKβ-spectrum, eV	
	absolute values	relative values[a]	absolute values [b]	relative values [a]
Ia	9.39	0.0	2141.2	0.0
	10.03	0.64	2140.1	1.1
	11.28	1.89	2139.5(sh)	1.7
	12.62	3.23	2137.7	3.5
			2135.8(sh)	5.4
Ib	8.85	0.0	2141.3	0.0
	9.65	0.8		
			2138.9(sh)	2.4
	12.14(w)	3.29	2138.5	2.8
			2137.6(sh)	3.7
	13.58	4.73	2136.6	4.7
	14.48	5.63		
Ic			2141.7	0.0
			2140.2	1.5
			2138.5	3.2
			2136.0(sh)	5.7
Id			2141.6	0.0
			2140.6	1.0
			2138.4(sh)	3.2
			2137.7	3.9
			2136.4(sh)	5.2
Ie			2143.4	0.0
			2141.6(sh)	1.8
			2139.9	3.5
			2137.7	5.7
			2136.6	6.8
			2135.0(sh)	8.4
Ig	9.47	0.0	2142.9	0.0
	11.13	1.66	2141.6	1.3
	12.45	2.98	2140.0	2.9
	13.52	4.05	2138.6	4.3
			2137.0	5.9
			2131.0(w)	11.9
			2123.0(w)	18.9
Ii	9.0	0.0	2143.6(sh)	0.0
	9.58	0.58	2142.8(sh)	0.8
	11.6	2.6	2141.9	1.7
	12.36	3.36	2140.9(sh)	2.7
			2140.0	3.6
	13.64	4.64	2139.4	4.2
			2138.7	4.9

(continued overleaf)

TABLE 1 (continued)

Ii	14.65	5.65	2137.8	5.8
			2136.2	7.4
			2135.5(sh)	8.1
			2132.0(w)	11.6
			2129.0(w)	14.6
			2126.0(w)	17.6
			2124.0(w)	19.6
			2119.5(w)	24.1
IIa[c]	8.54[d]	0.0	2142.8	0.0
	9.18	0.64		
	9.66	1.12	2141.9	0.9
	10.32	1.78	2140.3	2.5
	11.77	3.23	2139.0	3.8
			2135.7(sh)	7.1
			2132.3(w)	10.5
IIc[e]	7.80	0.0	2141.2	0.0
	8.87	1.07		
	9.16	1.36		
	9.27	1.47		
	9.70	1.90	2139.3(sh)	1.9
	10.8	3.0	2138.6	2.6
	11.7	3.9	2136.8	4.4
	12.4	4.6		
	13.3	5.5		
	13.8	6.0	2134.6(sh)	6.6
	14.5	6.7		
	16.4	8.6	2131.8(w)	9.4
IIIa[f]	10.6	0.0	2140.1	0.0
	13.4–13.9	2.8–3.3	2138.2	1.9
	19.0	8.4	2128.1	12.0
IIIg[g]	9.0	0.0	2143.0	0.0
			2142.2(sh)	0.8
	10.6	1.6	2141.5	1.5
	11.1	2.1	2140.7	2.3
	11.8	2.8	2140.0	3.0
	12.4	3.4	2139.3(sh)	3.7
	13.0	4.0		
	15.1	6.1	2136.9(sh)	6.1
	16.9	7.9	2136.0	7.0
			2133.5(sh)	9.5
			2130.5(w)	12.5
			2122.3(w)	20.7
IIIi			2142.5(sh)	0.0
			2141.0(sh)	1.5
			2140.3(sh)	2.2
			2139.0	3.5
			2137.6(sh)	4.9
			2136.3(sh)	7.2
			2133.6(sh)	8.9
			2129.5(w)	13.0
			2125.0(w)	17.5
			2120.0(w)	22.5

TABLE 1 (continued)

IIIj			2140.8 2138.7 2137.3(sh) 2134.8 2129.2(w)	0.0 2.1 3.5 6.0 11.6
IIIl			2144.4(sh) 2143.4(sh) 2143.0 2141.5 2140.2 2138.5 2137.2 2136.0 2134.8(sh) 2132.4(sh) 2124.9(w) 2122.3(w)	0.0 1.0 1.4 2.9 4.2 5.9 7.2 8.4 9.6 12.0 19.5 22.1

NOTES : sh - shoulder, w - wide band . [a] in respect to IP_1 (PES data) or the most short-wave maximum (PKβ -spectra); [b] in the scale with K-level of phosphorus as a zero point; [c] PES data from [32] ; [d] calculated by Matsen equation (see text); [e] PES data from [36]; [f] PES data from [42], see also [43]; [g] PES data from [44]; UPE spectrum has been reassigned by us on the basis of PKβ -spectrum (see text)

and so the interaction of the latter with a (b_1-n_p)-orbital can be expected to be a second-order effect because of substantial difference in their IP's. That effect leads to a relatively small contribution of a σ-type MO in HOMO of the phosphines (Ia) and (IIa), being mainly a (b_1-n_p)-orbital (Table 3). At the same time, the similar interaction of a σ-type MO with a (b_1+n_p)-orbital results in the formation of two new MO's - the antibonding one which can be assigned as $(b_1+n_p-\sigma)$ and the corresponding bonding $(b_1+n_p+\sigma)$-MO (Fig. 3). The contribution of the (b_1+n_p)-MO in these MO's is equal to 40-60% (see Table 2).

So the four highest occupied MO's in the phosphines (Ia) and (IIa) can be assigned in accordance with MINDO/3 calculations and X-ray fluorescent data (in order of increase of corresponding IP's to (b_1-n_p)- with small σ-contribution, a_2-, $(b_1+n_p-\sigma)$- and $(b_1+n_p+\sigma)$-MO's (Fig. 3). Three of them containing the contribution of n_p can be expected to give the corresponding maxima A', A'' and B in the short-wave region of the PK_β-spectra of these compounds (Fig. 1,2). A similar order of higher occupied MO's can be expected to be realized in aryldialkylphosphines and some other compounds of the $C_6F_5PX_2$ type.

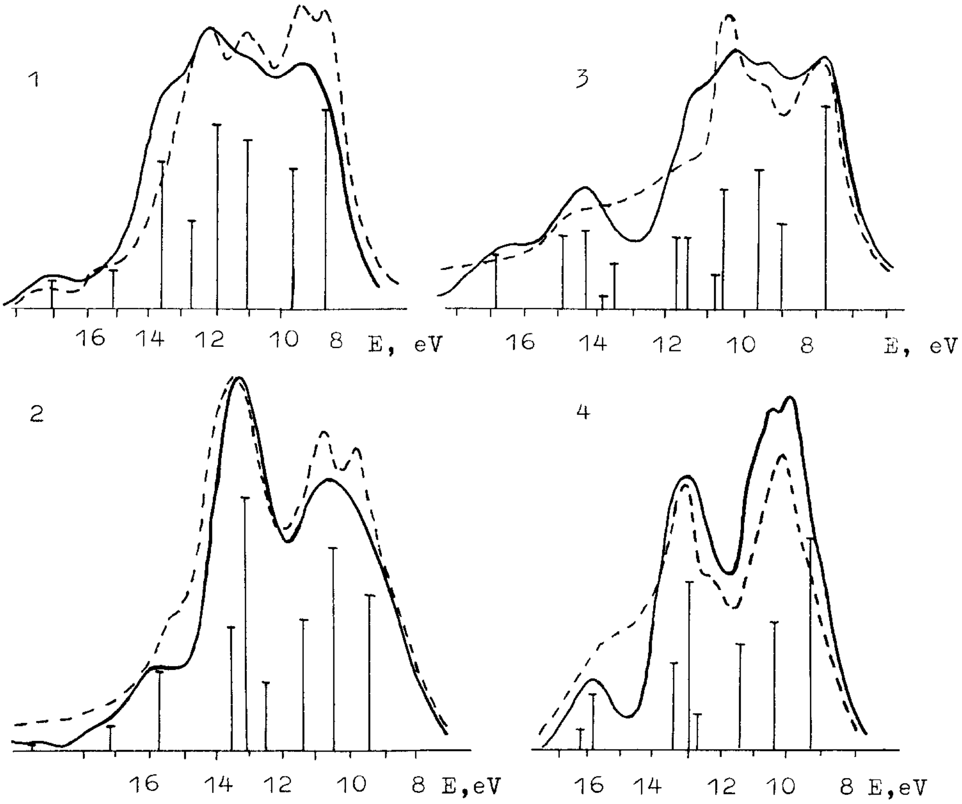

Fig.2. Experimental (– – –) and theoretical (——)(from MINDO/3 calculations data) PKβ -spectra of 1.$C_6H_5PH_2$ (IIa); 2. $C_6F_5PH_2$ (Ia); 3. $P(C_6H_5)_3$ (IIc); 4.$C_6F_5P(CH_3)_2$ (Ib). The calculated relative intensities of bands corresponding to 3p(P)-AO contributions in MO's have been shown as vertical lines.The halfwidth of the bonds in theoretical spectra is equal to 1.6 eV.

TABLE 2

First IP assignments for investigated phosphines from MINDO/3 calculations.

Compound	IP eV (PES)	Δ_{12} (PES)	Δ_{12} eV (MINDO/3)	IP (calcul.)	Assignment (main contributions)
Ia	9.39 10.03 11.28 12.62	0	0.01	9.20 9.21 10.34 11.30 11.32 11.50 12.37 13.12	a_2 b_1-n_p* σ(C-C), b_1+n_p(59%) σ(C-F) σ(C-C), b_1+n_p(36%) σ(C-C),σ(C-F) π(C_6F_5) (80%), p_z (7%) σ(P-H)
Ib	8.85 9.65 11.8 12.27	0	0.21	8.93 9.14 9.97 10.06 11.03 11.30 11.57 12.25 12.55	b_1-n_p* a_2 π(CH_3), σ(P-CH_3) b_1+n_p(68%), σ(C-C) b_1+n_p(28%), σ(P-CH_3) σ(C-C), σ(C-F) σ(C-F), σ(C-C) π(C_6F_5), p_z (5%) σ(P-CH_3)
IIa[a]	8.54[b] 9.18 9.66 10.32 11.77	0.64	0.69	8.58 9.27 9.62 10.38 10.83 11.85	b_1-n_p* a_2 σ(C-C), σ(C-H), b_1+n_p(42%) σ(C-H) σ(C-C), σ(P-H), b_1+n_p(53%) σ(P-H)
IIb[a]	8.31 8.83 9.15	0.52	0.85	8.40 9.25 9.44	b_1-n_p* a_2 σ(P-C), b_1+n_p(47%),

NOTES : * See Table 3 ; [a] From [32]; [b] From CTC data

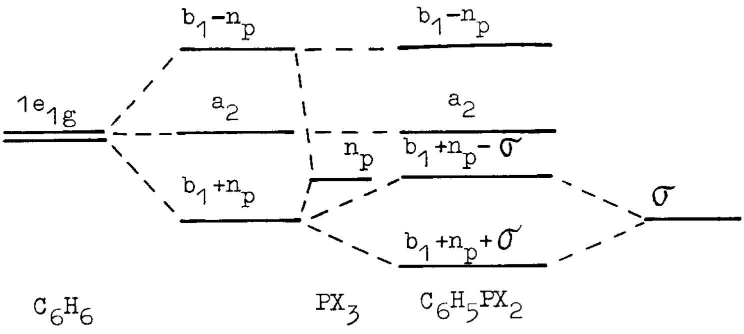

Fig.3. Orbital interaction diagram for $ArPX_2$.

TABLE 3
HOMO structure in investigated phosphines as calculated by MINDO/3 method.

Compound	Phosphorus atom				aromatic ring	
	P_s	P_x	P_y	P_z	$\sum C_z$	$\sum F_z$
Ia [a]	6	1	4	18	51	8
Ib	7	2	4	26	37	7
IIa	6	3	8	20	51	
IIb	6	3	8	26	39	
IIc [b]	5			32	39	
IIf	10	12		17	12	
IIIa	20 [c]			64 [d]		

NOTES : [a] the orbital is practically degenerated with a_2-MO; [b] at $\varphi = 15^\circ$; [c] lit. 17.1 [41]; [d] lit. 70 [41] .

Taking into account that the contribution of σ-type MO in HOMO is relatively small (Table 3) and the p_π-p_π-interaction between the π-system of the aromatic ring and the fluorine atoms of the C_6F_5-group in (Ia) does not lead to a substantial contribution of 2p (F)-AO in HOMO ($\sim$8% from MINDO/3 calculations) the effectiveness of p_π-p_π-interaction between LEP of phosphorus and aromatic π-system in (Ia) and (IIa) can be estimated by the corresponding Δ_{12} value as being the difference in energies of (b_1-n_p)- and a_2-MO's (see, e.g. [35]). The value Δ_{13} often used for the same purpose in the case of other heteroatoms, e.g. sulfur [25]*, cannot be used as a criterion of the effectiveness of a p_π-p_π-interaction between the phosphorus atom and the aromatic π-system as follows from the scheme (Fig. 3). Δ_{12} values for the phosphines (Ia), (Ib), (IIa), (IIb), have been determined from PES data and MINDO/3 calculations (Table 2). A comparative correlation diagram for vertical IP's for the compounds (Ia) and (IIa) together with the data for the model compound (IIIa) [42] has been shown on Fig. 4a.

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* For the more detailed discussion of the utility of values Δ_{12} and Δ_{13} as a criteria of p_π-p_π-interaction between LEP of a heteroatom and an aromatic π-system see [25] and references therein.

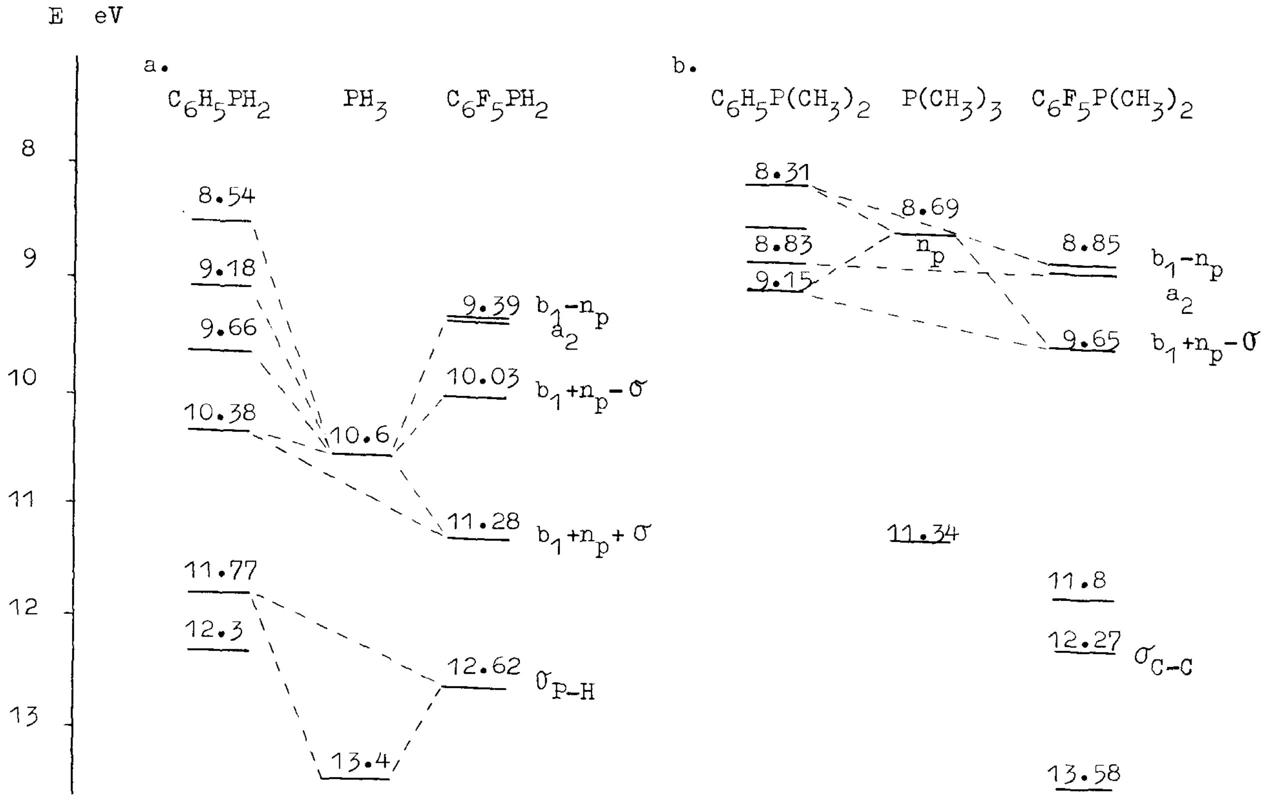

Fig.4. Correlation diagram of MO's in : a. $C_6H_5PH_2$, PH_3, $C_6F_5PH_2$;
b. $C_6H_5P(CH_3)_2$, $P(CH_3)_3$, $C_6F_5P(CH_3)_2$

The UPE spectral data for (IIa), used in the present work, have been taken from [32] but with one necessary correction. The literature PES data for this compound are rather controversial on the question of its first IP. Thus, the authors of [32] attribute the IP at 8.47 eV for (IIa) to an adiabatic one, estimating the vertical IP_1 as 9.18 eV. At the same time, the vertical IP_1 for this compound has been estimated in [37] as ~8.7 eV and in [39] as 8.88 eV. The MINDO/3 calculations leading to good agreement of calculated and experimental IP's of aromatic phosphines (Table 2, see also [41]) lead in the present work to the value of IP_1 = 8.58 eV, close to the corresponding calculated value in [41] (8.40 eV).

The IP_1 value of (IIa) could be estimated independently from the position of the charge-transfer band in the electronic absorption spectrum of the charge transfer complex (CTC) of (IIa) with TCNE. The corresponding band has been found by us to lie at 475 nm. Calculation by the Matsen equation [47] being the most universal for the various types of organic Π-donors [48] (parameters C_1 and C_2 have been taken from [49]) leads to the IP_1 (IIa) = 8.54 eV, which is close to those calculated by us and obtained from PES data in [37] (see above). At the same time, from our point of view, the IP at 9.18 eV [32] (~9.2 eV [37], 9.37 eV [39]) can be assigned to the a_2-orbital of the aromatic ring in accordance with [37,39] and our calculations (Table 2).

The data presented in Fig. 4a and Table 2 show the Δ_{12} value to be considerably smaller in the case of compound (Ia) than in the case of its hydrocarbon analogue (IIa) indicating the decrease of the effectiveness of p_{Π}-p_{Π}-interaction of the phosphorus LEP with the aromatic Π-system of the polyfluorinated ring. A broad band at 9.39 eV in the UPE spectrum of compound (Ia) appears to be complex, involving ionization from both (b_1-n_p)- and a_2-orbitals. This is in accordance with MINDO/3 calculations (Table 2) leading to almost degenerated (b_1-n_p)- and a_2-orbitals for this compound, whereas for its hydrocarbon analogue (IIa) $\Delta_{12(calc.)}=0.69$ eV (*cf.* $\Delta_{12(PES)}$ = 0.64 eV, Fig. 4a).

The effectiveness of p_{Π}-p_{Π}-interaction between the PX_2-group and the aromatic Π-system can be connected with the mesomeric effect of the former as a substituent in the aromatic or polyfluoroaromatic ring. An independent method for evaluation of the magnitude and the direction of that effect, namely ^{13}C NMR method has been used by us to test the above conclusion about the smaller effect of the p_{Π}-p_{Π}-interaction between the phosphorus LEP and the aromatic Π-system in the case of polyfluroaromatic phosphines. For that purpose the authors of [50] suggested as a criterion the $\Delta(\delta C_{para}-\delta C_{meta})$ value for the aromatic ring. We have recorded ^{13}C NMR spectra of a number of investigated phosphines of the type (I); the corresponding $\Delta(\delta C_{para}-\delta C_{meta})$ values are summarised in Table 4 for the comparable conditions (temperature, solvent). The NMR ^{13}C data for the phosphines of the type (II) are taken from [51] (^{13}C NMR spectrum of (IIa), obtained by us : 136.5 (C_{ipso}), 131.3 (C_{opto}), 124.7 (C_{meta}), 127.6 (C_{para}) ppm from TMS.

TABLE 4

Characteristics of interaction of phosphorus with aromatic π-system in investigated compounds from ^{13}C NMR spectra.

Compound	$\Delta(\delta C_{para}-\delta C_{meta})$ ppm	Compound	$\Delta(\delta C_{para}-\delta C_{meta})$ ppm
Ia	-0.6	Ii	-0.8
Ib	0.0	IIa	2.9
Id	1.5	IIb	-0.4*
Ie	3.1	IIc	0.1*
If	3.2	IIe	4.3*
Ig	0.7	IIf	3.6*
Ih	2.5	IIi	-0.9*

* From [51]

From the data of Table 4 the phenyl ring in (IIa) appears to be a Π-donor in respect to the PH_2-group. The introduction of five fluorine atoms into the ring (compound (Ia) leads to less effectiveness of Π-interaction between the PH_2-group and the aromatic Π-system* and to reverse the direction of the effect - the pentafluorophenyl ring behaves as a very weak Π-acceptor in respect to the PH_2-group. This is in accordance with PES data and completes the latter.

In the case of the phosphine (Ib) containing, in comparison with (Ia), methyl groups at the phosphorus atom instead of hydrogen, MINDO/3 calculation data indicate the practical identity of the structure of HOMO in (Ib) and (Ia) (Table 3) and the analogous order of higher occupied MO's (Table 2). The same conclusion follows also for the hydrocarbon analogues of compounds (Ia), (Ib), (IIa), (IIb) (Tables 2,3).

A correlation diagram for MO's in the compounds (Ib) and (IIb) together with the model compound (IIIb) has been shown in Fig. 4b (PES data for (IIb) and (IIIb) have been taken from [35] and [46] respectively). The Δ_{12} value for (Ib) cannot be determined from the obtained UPE spectrum of the latter. The broad band in the UPE spectrum of (Ib) at 8.85 eV corresponds probably to the ionizations from (b_1-n_p) - and a_2-MO's. The $\Delta_{12(calc.)}$ value for (Ib) is equal to 0.21 eV (Table 2) indicating that such a situation can take place.

The increase of the IP's corresponding to the higher occupied MO's in the compounds (Ia), (Ib) in respect to their hydrocarbon analogues (IIa), (IIb) following from the data of Tables 1,2 and Fig. 4a, 4b can be explained in terms of the less effectiveness of p_Π-p_Π-interaction between phosphorus LEP and aromatic Π-system (leading to the decrease of Δ_{12} value and hence the greater value of IP_1) and of the 'perfluoro effect' [53] leading to the stabilization of higher occupied MO's on the value ~0.5-0.8 eV (for Π-type MO's [53]). Thus, the increase of IP_2 (a_2-MO) of (Ia), (Ib) relative to

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* The latter is true even taking into account that the para-fluorine atom as a substituent leads to a decrease of chemical shift-charge ratio for C_{para} chemical shift in respect to the para-hydrogen atom (121 ppm per charge unit vs. 189 ppm per charge unit [52].

(IIa),(IIb) (Fig. 4a, 4b) indicates the influence of the perfluoro effect (cf. [25]), while the increase of IP_1 can be connected with both reasons. The greater value of IP_1 in polyfluoroaromatic phosphines can explain, in turn, their lower Π-donor ability.

The PK_β-spectrum of (Ib) has been shown in Fig. 1, and the comparison of X-ray fluorescent and PES data for (Ib) has been made in Table 1. Satisfactory agreement exists between the experimental and theoretical PK_β-spectra of this compound (Fig. 2). The short-wave maximum A in the PK_β-spectrum of (Ib) is not split and is the most intensive one in the spectrum, indicating in accordance with PES data (Fig. 4b) the small effect of the p_Π-p_Π-interaction of the phosphorus LEP with the Π-system of the polyfluoroaromatic ring in (Ib). The decrease of the effectiveness of such interaction in this compound with respect to its hydrocarbon analogue (IIb) follows also from ^{13}C NMR spectral data (Table 4).

The value of the resonance integral $H_{b_1 n_p}$ can be used also as an independent criterion for the evaluation of the effectiveness of the p_Π-p_Π-interaction between the LEP of the phosphorus atom and the Π-system of the aromatic and polyfluoroaromatic ring. The values of $H_{b_1 n_p}$ for the compounds (Ia), (Ib) and their hydrocarbon analogues (IIa), (IIb) have been calculated by us by a method similar to those in [25]. It has been of interest to compare the observed effect of the change of the effectiveness of the p_Π-p_Π-interaction between the LEP of the heteroatom and the Π-system of the polyfluoroaromatic ring in the derivatives of phosphorus, with the analogous effects for the derivatives of other heteroatoms. In the Table 5 the $H_{b_1 n_x}$ (X = N, P, O, S), Δ_{12} and $\Delta(\delta C_{para} - \delta C_{meta})$ for the compounds of $ArMX_n$ type ($Ar = C_6H_5, C_6F_5$; M = N, P, O, S; X = H, CH_3; n = 1, 2) have been shown.

As follows from the data of Table 5, the observed tendency to a less effective p_Π-p_Π-interaction of the LEP of the heteroatom with the Π-system of the pentafluorophenyl ring compared to the phenyl one is rather common for various heteroatoms. This tendency, in turn, appears to be one of the important factors

TABLE 5

Characteristics of p_{π}-p_{π}-interaction of heteroatoms with the aromatic system for the $ArMX_2$ derivatives (Ar = C_6H_5, C_6F_5; M = N, P, O, S; n = 1,2)

Compound	$H_{b_1 n_m}$ eV	Δ_{12}, eV	$\Delta(\delta C_{para} - \delta C_{meta})$ ppm
$C_6H_5NH_2$	-1.88	1.10 [54]	-10.8 [a]
$C_6F_5NH_2$	-1.42	0.80 [54]	-8.7
$C_6H_5PH_2$	-1.20	0.64	2.9
$C_6F_5PH_2$	-0.79	0.0	-0.6
C_6H_5OH	-1.67	0.72 [54]	-8.75 [a]
C_6F_5OH	-0.70	0.17 [55]	-6.3
C_6H_5SH	-1.20	0.97 [56]	-3.9 [a]
C_6F_5SH	-0.62	0.48 [25]	-3.2
$C_6H_5N(CH_3)_2$	-1.38 [b]	1.34 [b]	-12.3 [a]
$C_6F_5N(CH_3)_2$	-0.65 [b]	0.45 [b]	-5.1 [a]
$C_6H_5P(CH_3)_2$	-0.87	0.52	-0.4 [a]
$C_6F_5P(CH_3)_2$	-0.54	0.0 (0.21 [c])	-0.1
$C_6H_5OCH_3$	-1.10	0.79 [55]	-9.0 [a]
$C_6F_5OCH_3$	-0.34	0.0 [55]	-5.2
$C_6H_5SCH_3$	-1.27	1.21 [57]	-3.8 [a]
$C_6F_5SCH_3$	-0.46	0.66 [25]	-0.9

NOTES : [a] From [51] , [b] From CTC , [c] Calculated by MINDO/3 (Table 2)

determining an increase of the first IP and the degree of HOMO localization on the heteroatom (in particular, on phosphorus) in polyfluoroaromatic compounds containing heteroatoms compared to the corresponding hydrocarbon analogues, and so modifying the reactivity of the former in reactions occurring with the participation of frontier electron density.

The substantial increase of IP's in polyfluorinated phosphines of type (I) with respect to their hydrocarbon analogues of type (II) mentioned above (Fig. 4a, 4b) must be noticed to take place, even in the case of localization of corresponding MO's mainly on the substituent X. An interesting example of such an effect has been found by us for the compounds (Ii) and

(IIi). The HOMO in the compound (IIi) has been known to be localized on the nitrogen atoms [39] ; the PK$_{\beta}$-spectra of (Ii) and the model compound (IIIi) lead to the same conclusion for these compounds (Fig. 7 ; see also Table 1). The short-wave maxima in the PK$_{\beta}$-spectra of (Ii) and (IIIi) have relatively low intensity (Fig. 7), indicating the small contribution of 3p(P)-AO in the corresponding higher occupied MO's. In this case the higher occupied MO's in (IIIi) must be localized mainly c the nitrogen atoms and the similarity of the PK$_{\beta}$-spectra (short-wave region) of (IIIi) and (Ii) allow us to extend this conclusion to the compound (Ii).

Fig. 5b is the correlation diagram of MO's in (Ii) and (IIi) (PES data for (IIi) have been taken from [39]). The assignment of the UPE spectrum of (Ii) has been made by us on the basis of its PK$_{\beta}$-spectrum (Table 1) leading to the analogous assignment with those for the hydrocarbon analogue [39]. From the PES data (Fig. 5a) it follows that the introduction of fluorine atoms in the aromatic ring of (IIa) leads to a significant ($\sim$1.5 eV) increase of IP$_{1}$, in spite of the localization of HOMO on nitrogen atoms not bonded with the pentafluorophenyl ring. The analogous increase has been observed for the next IP's (Fig. 5a). As a possible reason of that effect, the substantial increase of positive charge on nitrogen atoms under the influence of pentafluorophenyl groups can be suggested. Recently the ability of pentafluorophenyl groups to change the charge on nitrogen atoms not bonded with the former has been shown by us in a series of aryl- and polyfluoroaryl-N,N-dichlorosulfamides and -amides [58].

It must be noticed that the scheme of MO interaction in arylphosphines (Fig. 3) has been considered in the present work with a suggestion that the molecules of (Ia), (Ib), (IIa) and (IIb) exist in the conformation facilitating the p_{Π}-p_{Π}-interaction between the LEP of the phosphorus atom and the aromatic Π-system (see [34]). A more complicated situation is observed in triarylphosphines (Ic), (Id), (IIc). Molecules of that type of compound are known to possess, both in solid [59] and gaseous [60] states, the "propeller" conformation making

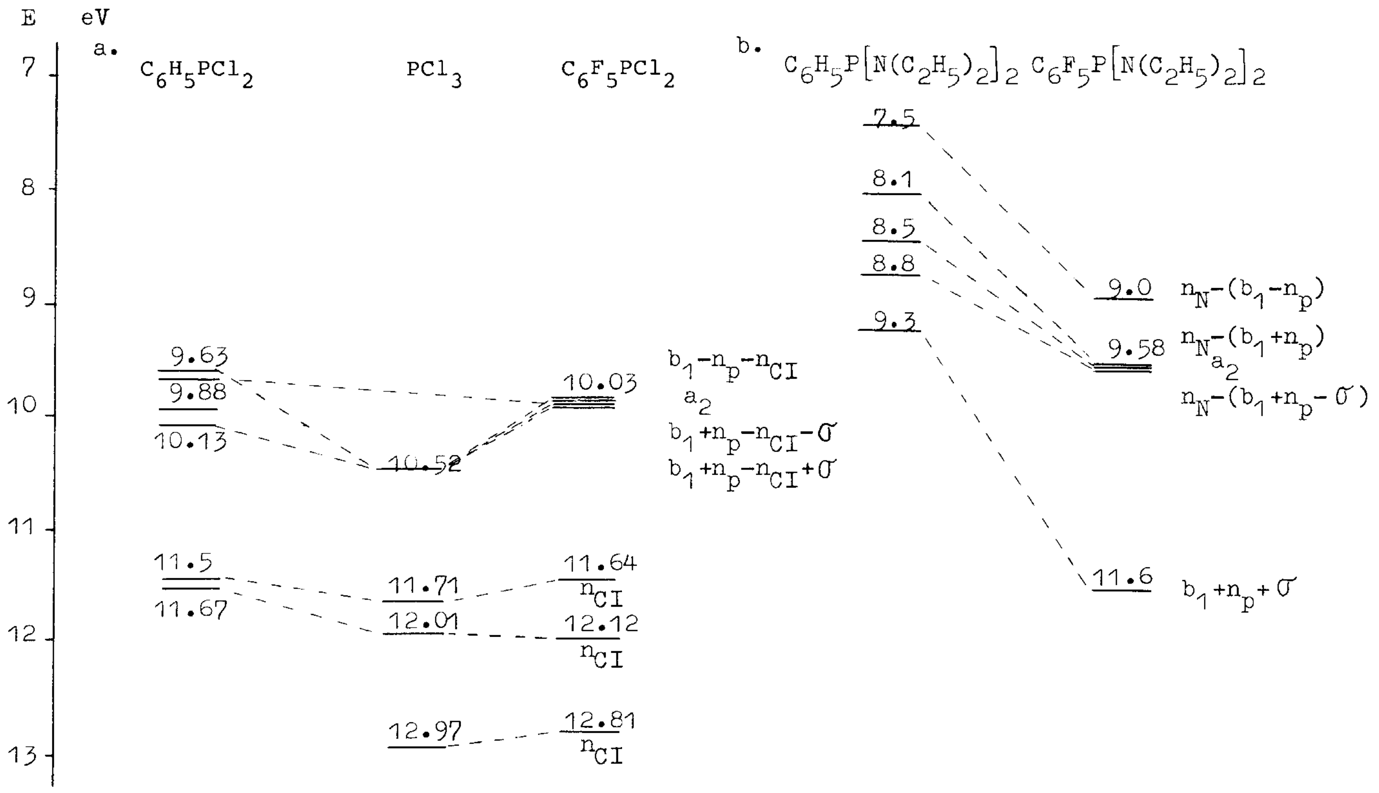

Fig.5. Correlation diagram of MO's in : a. $C_6H_5PCl_2$, PCl_3, $C_6F_5PCl_2$;
b. $C_6H_5P[N(C_2H_5)_2]_2$, $C_6F_5P[N(C_2H_5)_2]_2$

the p_{Π}-p_{Π}-interaction between the LEP of the phosphorus atom and the Π-system of aryl substituents unfavourable. But the analysis of the UV spectra of triarylphosphines does not exclude the possibility of such interaction [7].

The MINDO/3 calculations of the (IIc) molecule for the various values of the ring rotation angle ϕ* show that the contribution of the (b_1-n_p)-orbital in HOMO of that compound changes from ~80% ($\phi = 0^o$) up to ~60% ($\phi = 90^o$). With the increase of ϕ the b_1-orbital contribution in HOMO of (IIc) substantially decreases, whereas the n_p-contribution remains almost constant (35-45%), and the σ-type orbital contribution (mainly σ_{C-C}) is increased. These calculations do not allow us to assign the second IP for this compound to a_2-type orbital, showing the considerable mixing of the latter with σ_{C-C}-orbitals (but not with 3p(P)-AO; the latter fact follows as from the calculation data from the comparison of UPE and PK_{β}-spectra of (IIc) (Table 1), because the bands in the UPE spectra in the range 8.8-9.3 eV do not correspond to any maximum in the PK_{β}-spectrum of (IIc). A similar picture is observed in MINDO/3 calculation data for the polyfluorinated analogues of (IIc) - compounds (Ic) and (Id). Hence the Δ_{12}value for this type of compound does not characterize the p_{Π}-p_{Π}-interaction between the LEP of the phosphorus atom and the Π-system of the aromatic ring.

In Fig. 1 the PK_{β}-spectra of triarylphosphines (Ic), (Id) and (IIc) are represented (see also Table 1). The experimental and theoretical PK_{β}-spectra of (IIc) at $\phi = 15^o$ are in good agreement, as in shown in Fig. 2. The comparison of the experimental and theoretical PK_{β}-spectra of (IIc) (Fig. 2) shows that maximum A in the experimental spectrum corresponds to the HOMO of Π-type with complex structure. The calculated contribution of 3p(P)-AO in HOMO (~32%) seems to be somewhat overestimated taking into account the intensity of maximum A in

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* Bond lengths and bond angles have been taken from [59]; the ϕ values have been taken for the range 0^o-90^o. At $\phi = 90^o$ the phosphorus LEP is coplanar with the aromatic ring plane.

the theoretical and experimental spectra (Fig. 2). The latter, in comparison with the intensity of that maximum in the PK_β-spectra of (IIIa) and (IIIk) (Fig. 1) indicates that the considerable delocalization of HOMO in (IIc) on the phenyl groups takes place as a result of the p_Π-p_Π-interaction of LEP of the phosphorus atom with aromatic Π-systems. The alternative explanation of the low intensity of maximum A in the PK_β-spectrum of (IIc), namely the rehybridization of phosphorus AO leading to the increased s-character of its LEP in comparison with those in (IIIk) seems to be rather unsatisfactory taking into account the proximity of valence angles C-P-C in (IIc) and (IIIk) [17,59]. The stepwise replacement of phenyl groups in (IIc) by pentafluorophenyl ones (compounds (Ic) and (Id), Fig. 1) leads to the increase of HOMO localization on the phosphorus atom, as follows from the increase of intensity of the most short-wave maximum A' in the PK_β-spectra of the latter compounds, with respect to those of maximum A in the PK_β-spectra of (IIc) (Fig. 1).

In the PK_β-spectra of the series of compounds (IIc)-(Ic)-(Id) the long-wave shift of the position of maximum C in the range $\sim$0.7 eV has been observed (Fig. 1), indicating the action of the perfluoro effect on the corresponding MO's assigned according to MINDO/3 calculation to the group of σ-bonding MO's.

As the MINDO/3 calculations adequately reproduce IP_1 values (IP_1 of compound (IIc) is equal to 7.94 eV (calculated), 7.88 eV (UPE) [32], 7.92 eV (UPE) [33], see also Table 2), it has been of interest to evaluate in this way IP_1 of compound (Id). The corresponding calculated IP_1 appeared to be equal to 8.25 eV. That value led us to expect compound (Id) to form a CT(with TCNE with a charge transfer band position at $\sim$530 nm (according to the Matsen equation). At the same time, as has been recently shown by us, the electronic absorption spectrum of the solution of (Id) with TCNE in CH_2Cl_2 does not show any charge transfer bands at all [26]. This fact may be connected with HOMO's predominant localization on phosphorus of that compound (see Fig. 1) bearing a substantial positive charge (see below), and on positively charged carbon atoms.

Differences in the characteristics of higher occupied MO's between the phosphines of type (I) and type (II), determined by the influence of pentafluorophenyl groups, could be expected to diminish, as in the case of corresponding sulfur compounds [25], when the substituent X is capable of effective p_{π}-p_{π}-interaction with phosphorus LEP. Such interactions can be realized, e.g., in aryldihalophosphines. Thus in Fig. 5a the correlation diagram of MO in the compounds (If) and (IIf) together with the data for the model compound (IIIf) have been shown. The PES data for these compounds in comparison with their PK_{β} and ClK_{β}-spectral characteristics have been listed in Table 6. The assignment of UPE spectra in Fig. 5b has been made as in previous cases (Fig. 4a,4b,5a) on the basis of MINDO/3 calculations and K_{β}-spectra of investigated compounds (Table 1,3 ; in Table 3 the contribution of 3p(Cl)-AO in HOMO in (IIf) is ca. 20%). The effective p_{π}-p_{π}-interaction between the LEP's of phosphorus and chlorine leads to the change of n_p-orbital in the scheme of Fig. 3 for the compounds (If) and (IIf) by the antibonding combination of LEP's $(n_p - n_{Cl})$ (Fig. 5b ; cf. the data for arylsulfenylchlorides [25]). The corresponding bonding combination $(n_p + n_{Cl})$ has too low energy (IP > 14 eV) to interact effectively with the aromatic π-system.

From the data of Fig. 5b it follows that the Δ_{12} value in aryldichlorophosphines (If) and (IIf) cannot be determined from the obtained UPE spectra even in the case of the hydrocarbon analogue (IIf) (see [32,39]). All four MO's of the latter, shown in Fig. 3, lie within the range of ~0.5 eV (Fig. 5b), whereas in the compound (IIa) with the absence of effective p_{π}-p_{π}-interaction P-X, that range is equal to ~1.8 eV. In the case of the polyfluorinated compound (If) the broad band at 10.03 eV in the UPE spectrum appears to correspond to the group of occupied MO's being practically degenerated. The increase of the first IP's of (If) in respect to (IIf) is also considerably smaller than in the cases of compounds (Ia), (Ib), (Ii) relative to their hydrocarbon analogues (IIa), (IIb), (IIi) (Fig. 5b ; cf. Fig. 4a,4b,5a). Hence the energies and structure of higher occupied MO's in aryldichlorophosphines (If) and (IIf) can be concluded to be determined mainly by the effective p_{π}-p_{π}-interaction of LEP's of phosphorus and chlorine, and the influence of the nature of the aryl group (phenyl or pentafluorophenyl) is negligible with respect to the latter. A similar conclusion has been made by us recently in the series of divalent sulfur derivatives, namely arylsulfenyl chlorides [25], and aryl(arylethynyl)sulfides [63]. This fact should be noted not to exclude the influence of the nature of the aryl substituent on other characteristics of the electronic structure of (If) and (IIf) connected with their reactivity, e.g. on charge distribution in a molecule (see below).

In Fig. 6 PK_{β}- and ClK_{β}-spectra of chloro-containing phosphines (If), (IIf) and (IIIf) are represented together with the PK_{β}-spectrum of (Ie) (see also Table 6). The comparison of PK_{β}- and ClK_{β}-spectra of the compounds (If) and (IIf), shown on Fig. 6 in a common energy scale, on the basis of X-ray photoelectron data on inner level energies (see [61]) with PES data, and the corresponding spectra of (IIIf) made in Table 6 (see also Fig. 6), shows the UPE spectra of (If) and (IIf) to be correctly assigned. The energy difference between the maximum A in PK_{β}- and maximum B in ClK_{β}-spectrum is roughly equal to the energy difference between two groups of MO's, the first one corresponding to π-interaction of phosphorus with the substituents and the second one composed mainly of chlorine LEP's (Table 6, Fig. 5b,6). The structure of the short-wave region of the PK_{β}-and ClK_{β}-spectra of (If) and (IIf) is very close, indicating the proximity of structure of higher occupied MO's in these compounds determined mainly by p_{π}-p_{π}-interaction between LEP's of phosphorus and chlorine (Fig. 6). Because of the observed contribution of 3p(Cl)-AO's in the higher occupied MO's, the degree of localization of the latter on the phosphorus atom in (If) and (IIf) appears to be substantially smaller than in (Ia), (Ib), (IIa) and (IIb) (cf. the intensity of the corresponding short-wave maxima, Fig. 1,6). At the same time the relative width of maximum A in the

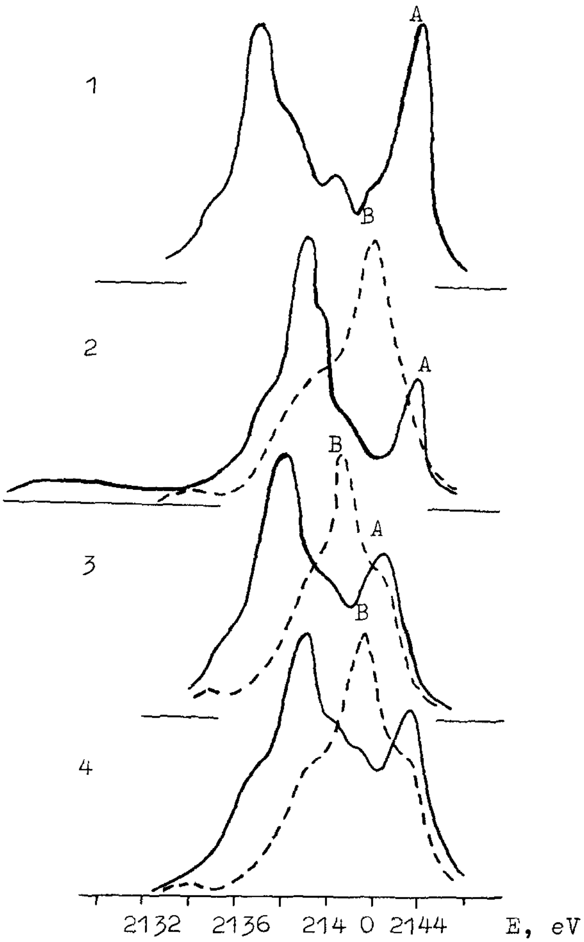

Fig.6. **PKβ** – (———) and ClK_{β} – (– – – –) spectra compounds :
1. $C_6F_5PF_2$ (Ie); 2. PCl_3 (IIIf); 3. $C_6F_5PCl_2$ (If);
4. $C_6H_5PCl_2$ (IIf) in common energy scale (see Table

PK_{β}-spectrum of (If) and (IIf) indicates its complex structure including the group of higher occupied MO's with close energies in accordance with PES data (Fig. 5b, 6, Table 6).

As the IP of fluorine LEP is ~4 eV higher than the chlorine one [65], the HOMO in (Ie) should be expected to be localized mainly on the phosphorus atom unlike (If). Indeed the PK_{β}-spectrum of (Ie) (Fig. 6) leads to the conclusion that p_{π}-p_{π}-interaction between phosphorus and fluorine LEP's is negli-

TABLE 6

Vertical ionization potentials and the energies of corresponding X-ray transitions in Kβ -spectra of investigated chloro- and sulfur containing phosphines.

Compound	IP's (from PES data), eV		The corresponding maxima in PKβ-spectrum, eV		in ClKβ-spectrum, eV		in SKβ -spectrum, eV	
	absolute values	relative values [a]	absolute values [b]	relative values [a]	absolute values [b]	relative values [a]	absolute values [c]	relative values [a]
If	10.03	0.0	2142.4	0.0	2142.4(sh)	0.0		
	11.64	1.61			2140.5	1.9		
	12.12	2.09						
	12.81	2.78	2139.7(sh)	2.7	2139.5(sh)	2.9		
	14.07	4.04	2138.0	4.4				
			2135.9(sh)	6.5				
					2134.6(sh)	7.8		
IIf [d]	9.63	0.0	2143.7	0.0	2143.7(sh)	0.0		
	9.88	0.25						
	10.13	0.5						
	11.50	1.87	2141.6(sh)	2.0	2141.6	2.0		
	11.67	2.04						
			2140.0(sh)	3.7	2140.0(sh)	3.7		
			2139.0	4.7				
			2137.0(sh)	6.7				
					2133.6(w)	10.1		
IIIf [e]	10.52	0.0	2143.5	0.0	2143.5 [f]	0.0		
	11.71	1.19						
	12.01	1.49			2141.8	1.7		
	12.97	2.45						
			2140.2(sh)	3.3				
	14.24	3.72	2139.2(sh)	4.3	2139.2(sh)	4.3		
	15.22	4.70	2138.9	4.6				
			2137.6	5.9				
	18.85	8.33	2136.0(sh)	7.5	2134.0(w)	9.5		
			2128.5(w)	15.0				

Ih	9.4	0.0	2143.2	0.0			2469.1(sh)	0.0
	9.9	0.5					2467.9(sh)	1.2
	10.15	0.75						
	11.8	2.4	2141.0	2.2			2467.1	2.0
	12.21	2.81						
	13.7	4.3	2139.3	3.9				
	14.2	4.8	2138.0	5.2				
	14.75	5.35						
							2463.1(sh)	6.0
							2462.2	6.9
			2135.4(sh)	7.8				
							2459.8(sh)	9.3
			2131.2(w)	12.0				
			2124.0(w)	19.2				
IIIh			2144.0	0.0			2468.8(sh)	0.0
			2143.2	0.8			2468.0(sh)	0.8
							2467.2	1.6
			2141.8	2.2				
			2139.4(sh)	4.6				
			2138.6	5.4				
							2463.1(sh)	5.7
							2462.3	6.5
			2135.6	8.4				
			2124.6(w)	19.4				

NOTES :

sh - shoulder, w - wide band

[a] In respect to IP_1 (PES data) or the most short-wave maximum in corresponding $K\beta$ -spectrum, [b] In scale with K-level of phosphorus as a zero point, [c] In the scale with K-level of sulfur as a zero point, [d] PES data from [32] , [e] PES data from [61] ,see also [62], [f] The corresponding maximum is not resolved (Fig.6)

gible. Maximum A in the PK_β-spectrum of that compound is relatively narrow and the most intensive in the spectrum indicating the substantial localization of HOMO on the phosphorus atom, facilitating from the point of view of frontier orbital theory [27] the orbital-controlled electrophilic attack on this atom while the charge-controlled one is unfavourable because of effective positive charge on the latter (see below, Table 7).

In the case of group V and group VI heteroatoms as substituents at phosphorus in compounds of the (I) and (II) type, the nature of interaction and the structure of the PK_β-spectrum become considerably more complicated (Fig. 7). The influence of the pentafluorophenyl group on the structure of upper occupied MO's in these compounds is relatively weak with respect to the model phosphines of type (III) (cf. PK_β-spectra of compounds (Ig)-(IIIg); (Ii)-(IIIi). In this case the degree of higher occupied MO's localization on phosphorus can be determined by the effectiveness of the p_Π-p_Π-interaction between the LEP's of phosphorus and the heteroatom. Thus, the phosphorus 3p-AO contribution to HOMO is increased in a sequence (Ii) $<$ (Ih) $<$ (Ig), which corresponds to IP_1 increase for HX compounds of that series : $HN(C_2H_5)_2$ (8.51 eV [66]) $<$ HNCS (9.94 eV [67]) $<$ CH_3OH (10.94 eV [68]). Taking into account the IP_1 value of compound (Ia) (Table 1) characterising the C_6F_5P-fragment to the same approximation, it is possible to conclude that in compound (Ii), HOMO must be mainly localized on nitrogen and that the pentafluorophenyl group at phosphorus must promote such localization, in (Ii) with respect to (IIi), because of the increase of IP_1 of the ArP-fragment and hence the energy difference between HOMO's of ArP- and $N(C_2H_5)_2$ -fragments (cf. IP_1 of (Ia) and (IIa), Table 1).

Hence, the electrophilic attack on (Ii) can be expected to take place on a nitrogen atom (as charge-controlled because of positive charge on phosphorus atom (see below) as orbital-controlled). Experimentally the protonation of (Ii) in acid media leads to only the N-protonated form [3].

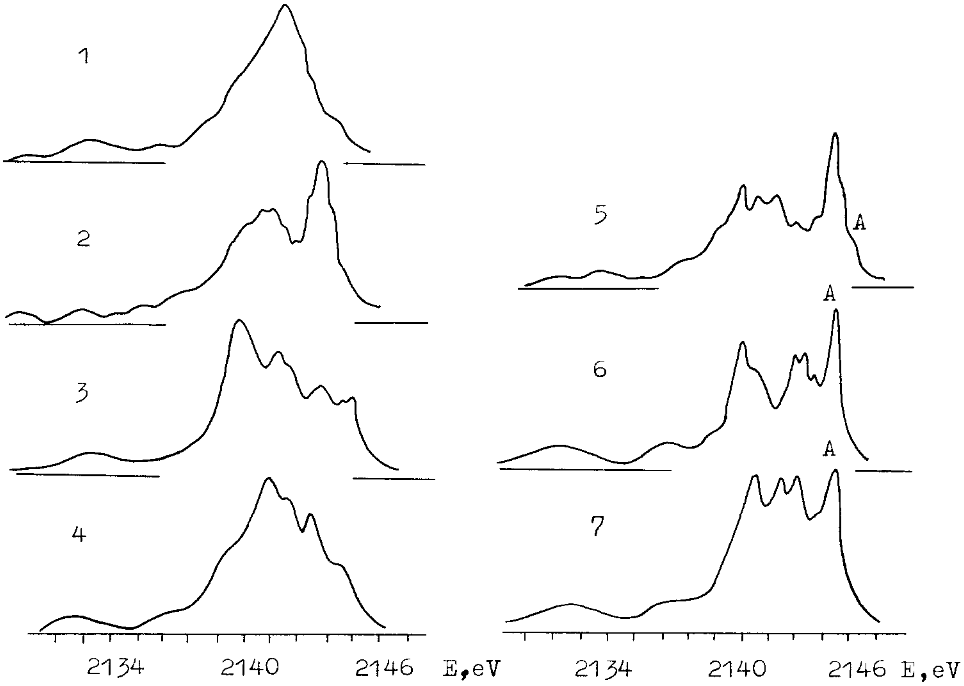

Fig.7. PKβ -spectra of investigated phosphines : 1. $P[N(C_2H_5)_2]_3$ (IIIi), 2. $C_6F_5P[N(C_2H_5)_2]_2$ (Ii), 3. $P(NCS)_3$ (IIIh), 4. $C_6F_5P(NCS)_2$ (Ih), 5. $P(OC_6F_5)_3$ (IIIl), 6. $P(OCH_3)_3$ (IIIg) 7. $C_6F_5P(OCH_3)_2$ (Ig)

At the same time the narrow and intensive maximum A in the PK_β-spectra of compounds (Ig) and (IIIg) (Fig. 7) indicates a weakly bonded HOMO mainly localized on phosphorus, which is also consistent with the fragmentary approach used above and the data on the reactivity [1,30].

The PK_β-spectrum of (IIIg) (Fig 7) permits us to reassign the UPE spectrum of this compound obtained in [44]. The good agreement between the relative MO energies determined from PES and X-ray fluorescent data (Table 1) must be noticed. From the data of Table 1, it follows that the band at 9.0 eV is evidently complex, including the ionization from n_p and n_o with some contribution of 3p(P)-orbitals. The further bands have been assigned by us to the following orbitals : n_O + some 3p(P)-contribution (10.6 eV), σ_{P-O} (11.1 and 11.8 eV), σ_{C-O}+ 3p(P)-contribution (12.4 and 13.0 eV).

It is interesting to note that replacement of CH_3-groups in compound (IIIg) by pentafluorophenyl ones (compound (IIIl)) results in a considerable delocalization of HOMO from phosphorus on the C_6F_5O-fragment (Fig. 7). In this case, the intensity maximum A in the PK_β-spectrum of compound (IIIl), corresponding to a 3p(P)-AO contribution to HOMO, appears to be lower than for its hydrocarbon analogue (IIIk) (Fig. 7, cf. 28). That fact is in contrast with the usual influence of the pentafluorophenyl group on HOMO localization with respect to the phenyl one (cf. e.g., PK_β-spectra of (Id) and (IIc), Fig. 1).

For the analysis of HOMO localization in compound (Ih), being an intermediate case with respect to (Ii) and (Ig), we have used also the SK_β-spectra of (Ih) and the model compound (IIIh) (Fig. 8, Table 6) together with the SK_β-spectra of KSCN (to model the SCN-group) and thiourea (to model the N=C=S-group). The structures of the SK_β-spectra of (Ih) and (IIIh) are identical to those of thiourea being indicative of the isothiocyanate structure of (Ih) and (IIIh). A short-wave maximum A in the SK_β-spectra of (Ih) and (IIIH) (Table 6) corresponding to a 3p(S)-AO contribution in HOMO appears as a shoulder of low intensity (Fig. 8). Taking into account that this maximum corresponds to the contribution of two sulfur atoms in HOMO it follows that the degree of localization of the latter on each of these atoms is relatively small. So the sulfur atoms are the preferential center of charge-controlled electrophilic attack on the molecules (Ih) and (IIIh) [the negative charge on the sulfur atom in these compounds is greater than in KSCN as follows from X-ray SK_α-shifts, -0.07 (Ih) and (IIIh) and -0.05 eV respectively; the value of charge on the sulfur atom for the latter has been reported earlier as -0.59 e [69]] but unfavourable for an orbital-controlled one. The positively charged phosphorus atom in (Ih) and (IIIh)

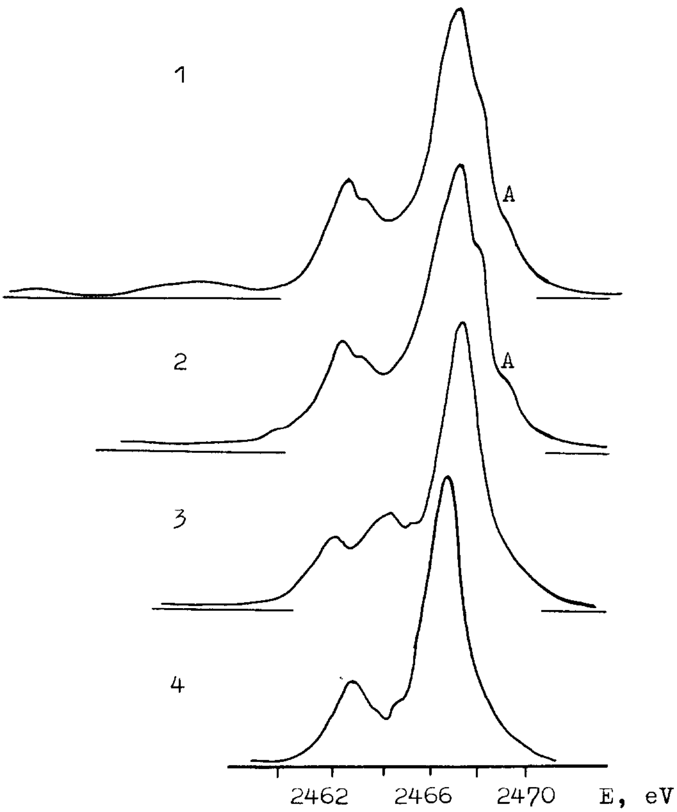

Fig.8. SKβ -spectra of compounds : 1. $P(NCS)_2$ (IIIh), 2. $C_6F_5P(NCS)_2$ (Ih), 3. KSCN, 4. $(NH_2)_2CS$

(Table 7) can be attacked by an electrophile obviously as a result of orbital-controlled reaction (see PK_β-spectra, Fig. 7). A somewhat greater (than for (Ig) and (Ii)) value $\Delta(\delta C_{para}-\delta C_{meta})$ for (Ih) (Table 4) can also indicate partial delocalization of HOMO in (Ih) on the pentafluorophenyl ring as a result of p_Π-p_Π-interaction of the latter with the $-P(NCS)_2$-fragment.

In Tables 1 and 6 the PES data for the compounds (Ig) and (Ih) respectively have been represented. The comparison of them with relative energies of MO's obtained by the X-ray fluorescent method (Table 1,6) as in cases of other investigated phosphines (see above) provides a possibility for the

TABLE 7

The charge characteristics of phosphorus atoms (ΔPKα and $q_{cov.}$(P)) in investigated phosphines.

Compound	ΔPKα eV	q_{cov}(P) e	q(P) calcd. MINDO/3	Compound	ΔPKα eV	q_{cov}(P) e	q(P) calcd. MINDO/3
Ia	0.02(2)	0.02(2)	0.06	IIc	0.02(1)	0.02(1)	0.03
Ib	0.07(2)	0.06(2)	0.08	IIf	0.25(1)	0.20(1)	0.58
Ic	0.01(3)	0.01(3)		IIIa	-0.08(3)	[a]	-0.04
Id	0.17(1)	0.14(1)		IIIe			0.28
Ie	0.45(3)	0.35(3)		IIIf	0.36(1)	0.28(1)	0.92
If	0.25(1)	0.20(1)		IIIg	0.48(1)	0.37(1)	
Ig	0.52(1)	0.41(1)		IIIh	0.52(1)	0.41(1)	
Ih	0.49(1)	0.38(1)		IIIi	0.53(1)	0.42(1)	
Ii	0.31(1)	0.25(1)		IIIj	0.00(1)	0.00(1)	
IIa	-0.08(1)		-0.06	IIIk	0.52(1)[b]	0.41(1)	
IIb			-0.02	IIIl	0.53(1)	0.42(1)	

NOTES : [a] The dependence of ΔPKα on $q_{cov.}$(P) has been precisely determined only for the positive ΔPKα value; in the range of negative values,the slope of the curve is 'steeper' (similarly to the dependence of ΔClKα on $q_{Pauling}$(Cl) [58]); [b] Lit. +0.54 eV [28].
The experimental error in the last sign of the values of ΔPKα and $q_{cov.}$(P) has been shown in brackets.

assignment of UPE spectra of these compounds in spite of their relatively complex structure. The contributions of heteroatoms in higher occupied MO's in (Ig) and (Ih) follow from the data of Tables 1 and 6 in comparison with the intensities of corresponding maxima in K_{β}-spectra (Fig. 7,8).

An important characteristic of the electronic structure of investigated phosphines, substantially determining their relative reactivity in reactions involving HOMO electron density (because of considerable phosphorus AO contribution in HOMO), is the value of the charge on phosphorus. On the basis of the known dependence of phosphorus X-ray K_{α}-shift on charge in covalent radius $q_{cov.}$(P) [29], we have determined the $q_{cov.}$

(P) values of investigated phosphines, presented with the values of PK_α-shifts and calculated charges on phosphorus by MINDO/3 method in Table 7. From the data of Table 7 it follows that in the investigated phosphines the phosphorus atoms possess as a rule the effective positive charge. The pentafluorophenyl group, as follows from the comparison of charge values of phosphorus in corresponding phosphines of types (I) and (II), shows a considerable total electron-withdrawal effect with respect to the phosphorus atom, and the analogous influence of phenyl group is near to zero (Table 7, compounds (Id) and (IIc)). It should be noted that the charge on phosphorus in (IIc) (and, hence, the influence of the phenyl group on the charge state of phosphorus) according to the data reported by various authors [70-73] varies in the range from -0.42 e up to +0.30 e. The calculated values of charges on phosphorus by the MINDO/3 method are in good agreement with the experimental (Table 7) in case of the absence of P-E bonds ($E \neq H, C$) in the investigated phosphine (the calculated charge on phosphorus in (IIc) is also close to zero (Table 7)).

A substantial influence on the charge of the phosphorus atom has been found by us for the substituents containing heteroatoms (Table 7). e.g. the methoxy group acts as a strong electron-acceptor with respect to phosphorus. That can be explained by the little effect of the p_π-p_π-interaction between the LEP's of phosphorus and oxygen or nitrogen leading to the influence of oxygen- and nitrogen-containing groups on the charge on phosphorus in accordance with their inductive effect (being electron-withdrawing).

Recently, investigation of the covalency of the N-Cl bond in polyfluoroaromatic N,N-dichlorosulfamides and -amides together with their hydrocarbon analogues provided by us, has shown that the presence of the pentafluorophenyl group in these molecules leads to substantial diminishing of the ionic character of the N-Cl bonds [58]. It seemed interesting to note that in the aryldichlorophosphines (If) and (IIf) the opposite situation has been observed. The charges on the phosphorus atoms in these compounds are practically equal (Table 7), whereas the estimation of q(Pauling) (Cl) in these compounds by the method described in [58] leads to the values $\sim$-0.6 e (If) and $\sim$-0.3 e (IIf), indicating the P-Cl bond as being considerably more ionic in the case of the polyfluoroaromatic phosphine (If). This result explains, for example, the fact that (If) hydrolyzes in the air considerably faster than its hydrocarbon analogue (IIf). Thus, maintaining a sample of (If) (thin layer) in the air during $\sim$0.5 min followed by placing of this sample in a vacuum leads to the absence of chlorine K-lines in the X-ray fluorescent spectra (indicating practically complete hydrolysis) while the hydrocarbon analogue (IIf) under the same conditions is unchanged.

The data of Table 7 allow us also to draw some conclusions about the possibility of d_{π}-p_{π}-interaction between phosphorus atoms and substituents at the latter in the investigated phosphines. It is known that the necessary condition for the existence of such an interaction consists in the presence of sufficient positive charge on phosphorus leading to a diminishing of the radius of the vacant 3d(P)-AO [74,75]. Hence the existence of a d_{π}-p_{π}-interaction of the phosphorus atom with substituents in compounds (Ia), (Ib), (IIa), (IIb), (IIc), (IIIa),)IIIj), where the charge on phosphorus is negative or close to zero, seems improbable. At the same time a certain d_{π}-p_{π}-conjugation may be supposed to exist for compound (Id), which shows, according to the $\Delta(\delta\ C_{para} - \delta\ C_{meta})$ value (Table 4), a certain π-donor effect of the pentafluorophenyl ring towards phosphorus in comparison with its hydrocarbon analogue (IIc), and has a considerable positive charge on phosphorus caused by pentafluorophenyl groups. d_{π}-p_{π}-Interaction seems also to play a certain role in compounds in which $q_{calcd.}(P) > q_{cov}(P)$ for compound (Id) (Table 7). Thus, the presence of 3d-electron density on phosphorus has been shown recently for the compound (IIIf) [62] being in accordance with the above condition.

The results of the present work on the electronic structure of polyfluoroaromatic phosphines, their hydrocarbon analogues, and model compounds, lead from our point of view to some conclusions about the nature of the influence of pentafluorophenyl groups on the characteristics of electronic structure and reactivity of the investigated compounds permitting explanations in terms of frontier orbital theory. The pentafluorophenyl group as a substituent with respect to the phenyl group possesses a reduced ability towards p_{Π}-p_{Π}-interaction with the LEP of the heteroatom bonded with it (Table 5) (in particular, with phosphorus LEP). The less effectiveness of that interaction together with the action of the 'perfluoro-effect' (connected with the appearance of positive charges on the centers of HOMO localization, i.e. carbon atoms of the pentafluorophenyl ring and the phosphorus atom) leads to an increase of the IP_1 of polyfluoroaromatic phosphines with respect to their hydrocarbon analogues in the range from ~ 0.4 up to ~1.5 eV (Table 1,6, Fig. 4a, 4b, 5a, 5b). The greater value of IP_1 together with HOMO localization mainly ($>$90%) on positively charged centers can be the reason for the reduced reactivity of polyfluoroaromatic phosphines in comparison with their hydrocarbon analogues in reactions determined by the Π-donor properties of phosphines. The use of the frontier orbital theory approach [27] leads also to the conclusion that in polyfluoroaromatic phosphines the charge-controlled electrophilic attack on the phosphorus atom is unfavourable because of the influence of the pentafluorophenyl group on the charge on phosphorus (Table 7), but the possibility of orbital-controlled electrophilic attack on the phosphorus atom remains because of greater localization of HOMO on the phosphorus atom in polyfluoroaromatic phosphines with respect to hydrocarbon analogues.

EXPERIMENTAL

UPE spectra have been recorded on the spectrometer designed at the Institute of Physics of the Leningrad state university. A resonance He I line with λ = 584 Å (21.21 eV) has been used as ionization source. The calibration of spectra has been made by Xe lines (12.13 and 13.43 eV). The accuracy of determination of IP's has been equal to ±0.02 eV (in case of the wide bands ±0.05 eV). X-ray fluorescent spectra have been recorded at 77 K on X-ray spectrometer "Stearate" using quartz (the rhombohedral plane as a crystal-analyser. The working regime of X-ray tube : voltage 8 kV, anodic current 0.6 A.As an exciting radiation for K-spectra of phosphorus, sulfur and chlorine AgL-radiation has been used. The samples for the X-ray spectrometer have been prepared by evaporating the investigated compounds at 10^{-5} torr on iridium or nickel plate maintained at 77 K or by putting a thin layer of the substance on chequered copper or nickel plate.

Quantum-chemical calculations by the MINDO/3 method have been performed using a set of quantum-chemical programs 'Viking' described in [76]. The parameters of the method correspond to those in [40,77], the data on bond lengths and bond angles of phosphines have been taken from [59,60,78,79]. The compounds (Ia), (Ib), (IIa), (IIb) have been calculated in conformation suggested for (IIa) in [34] showing the best agreement with the experimental data (charge on phosphorus, IP_1 value, the general view of PK_β-spectrum).

REFERENCES

1 G.A.Olah and C.W. McFarland, J.Org.Chem.,34 (1969) 1832

2 G.A.Olah and C.W. McFarland, J.Org.Chem., 36 (1971) 1374

3 G.G.Furin,S.A.Krupoder.A.I.Rezvuchin,T.M.Kilina and G.G.Yakobson, to be published

4 A.J.Birch,A.L.Hinde and L.Radom, J.Am.Chem.Soc., 102 (1980) 4074

5 R.L.DeKock, J.Am.Chem.Soc., 97 (1975) 5592

6 J.G.Verkade, Pure Appl.Chem., 52 (1980) 1131

7 G.V.Ratovsky,A.M.Panov,O.A.Jakutina,Ju.I.Suchorukov and E.N.Tsvetrov, Zh.Obshch.Khim., 48 (1978) 1520

8 G.V.Ratovsky,A.M.Panov,Ju.I.Suchorukov,O.A.Jakutina and E.N.Tsvetkov, Zh.Obshch.Khim., 49 (1979) 548

9 O.A.Jakutina,G.V.Ratovsky,Ju.L.Frolov,L.M.Sergienko and V.G.Rozinov, Teor.Eksp.Khim., 7 (1971) 514

10 I.P.Romm,E.M.Sadykova,E.N.Gur'yanova,I.D.Kolli and K.A.Kocheshkov, Dokl.Akad.Nauk SSSR, 195 (1970) 372

11 I.P.Romm,E.M.Sadykova,E.N.Gur'yanova and I.D.Kolli, Zh.Obshch.Khim., 43 (1973) 728

12 I.P.Romm,E.N.Gur'yanova, Zh.Obshch.Khim., 46 (1976) 445

13 H.Goetz,B.Klabuhn,F.Marschner,H.Juds and A.Wahid, Phosphorus, 2 (1973) 221

14 S.I.Pombrik,V.F.Ivanov,A.S.Peregudov,D.N.Kravtsov,A.A.Fedorov, and E.I.Fedin, J.Organomet.Chem., 153 (1978) 319

15 B.I.Stepanov,A.I.Bokanov and B.A.Korolev, Teor.Eksp.Khim., 4 (1968) 354

16 E.N.Tsvetkov,D.A.Bochvar and M.I.Kabachnik, Teor.Eksp.Khim., 3 (1967) 3

17 E.N.Tsvetkov and M.I.Kabachnik, Usp.Khim., 40 (1971) 177

18 E.N.Tsvetkov, Zh.Obshch.Khim., 45 (1975) 490

19 O.A.Raevsky,A.N.Vereshchagin,Ju.A.Donskaya,Ju.G.Chalitov, I.G.Malachova and E.N.Tsvetkov, Izv.Akad.Nauk SSSR,Ser. Khim., (1974) 453

20 O.A.Raevsky,A.N.Vereshchagin,Ju.A.Donskaya,J.G.Malachova, Ju.I.Suchorukov,E.N.Tsvetkov and M.I.Kabachnik, Izv.Akad. Nauk SSSR,Ser.Khim., (1976) 2243

21 V.A.Naumov,N.M.Zaripov and N.A.Gulyaeva, Zh.Strukt.Khim., 13 (1972) 917

22 J.E.Bissey and H.Goldwhite, Tetrahedron Lett., (1966) 3247

23 R.F. De Ketelaere and G.P.van der Kelen, J.Mol.Struct., 27 (1975) 363

24 G.N.Dolenko,S.A.Krupoder,L.N.Mazalov,L.I.Nasonova,G.G.Furin and G.G.Yakobson, Izv.Akad.Nauk SSSR,Ser.Khim., (1979) 343

25 B.G.Zykov,S.A.Krupoder,G.N.Dolenko,G.G.Furin,V.I.Chvostenko and G.G.Yakobson, Izv.Akad.Nauk SSSR,Ser.Khim., (1981) 1271

26 S.A.Krupoder,G.N.Dolenko,G.G.Furin,O.I.Andreevskaya and G.G.Yakobson, Izv.Sib.Otd.Akad.Nauk SSSR,Ser.Khim., (1981)(6) 119

27 G.Klopman, J.Am.Chem.Soc., 90 (1968) 223

28 Y.Takahashi, Bull.Chem.Soc.Japan, 45 (1972) 4

29 The X-ray spectra of molecules. Editor A.V.Nikolayev, Novosibirsk, Nauka Publishers, 1977, p.115,299

30 A.Meisel,G.Leonhardt,P.Sargan, X-ray spectra and chemical bonding. Kiev, Naukova Dumka Publishers, 1981,p.148,190

31 T.Koopmans , Physica, 1 (1933) 104

32 T.P.Debies and J.W.Rabalais, Inorg.Chem., 13 (1974) 308

33 M.A.Weiner,M.Lattman and S.O.Grim, J.Org.Chem., 40 (1975) 1292

34 H.Schmidt,A.Schweig and G.Mathey, Tetrahedron, 31 (1975) 1287

35 W.Schafer and A.Schweig, Ang.Chem.Int.Ed., 11 (1972) 836

36 K.Ostoja Starzewski and H.Bock, J.Am.Chem.Soc., 98 (1976) 8486

37 H.Bock, Pure Appl.Chem., 44 (1975) 343

38 V.V.Zverev and Ju.P.Kitaev, Usp.Khim., 46 (1977) 1515

39 D.E.Cabelli,A.H.Cowley and M.J.S.Dewar, J.Am.Chem.Soc., 103 (1981) 3286

40 R.C.Bingham,M.J.S.Dewar and D.H.Lo, J.Am.Chem.Soc., 97 (1975) 1285

41 H.Goetz,G.Frenking and F.Marschner, Phosph.Sulf.Rel.Elem., 4 (1978) 309

42 A.W.Potts and W.C.Price, Proc.Roy.Soc., 326A (1972) 181

43 G.N.Dolenko,S.A.Krupoder and L.N.Mazalov, Zh.Strukt.Khim., 20 (1979) 334

44 D.Betteridge,M.Thompson,A.D.Baker and N.R.Kemp, Anal.Chem., 44 (1972) 2005

45 H.Bock,G.Wagner and J.Kroner, Tetrahedron Lett., (1971) 3713

46 S.Cradock and E.A.V.Ebsworth, J.Chem.Soc.,Faraday Trans.II, 68 (1972) 934

47 S.H.Hastings,J.L.Franklin,J.C.Shiller and F.A.Matsen, J.Am.Chem.Soc., 75 (1953) 2900

48 J.Bendig and D.Kreysig, Z.Phys.Chem.(Leipzig), 258 (1977) 1176

49 R.S.Becker and E.Chen, J.Chem.Phys., 45 (1966) 2403

50 A.C.Boicelli,R.Danieli,A.Mangini,A.Ricci and G.Pirazzini, J.Chem.Soc,Perkin Trans.II, (1974) 1343

51 D.F.Ewing, Org.Magn.Res., 12 (1979) 499

52 J.Bromilow.R.T.C.Brownlee,D.J.Craik,M.Sadek and R.W.Taft, J.Org.Chem., 45 (1980) 2429

53 C.R.Brundle,M.B.Robin and N.A.Kuebler, J.Am.Chem.Soc., 94 (1972) 1466

54 T.P.Debies,J.W.Rabalais, J.Electron Spectr.Rel.Phen., 1 (1972) 355

55 J.P.Maier and D.W.Turner, J.Chem.Soc.,Faraday Trans.II, 69 (1973) 521

56 Progress in photonics. Editor F.I.Vilesov, Leningrad, Leningrad state university Publishers, 5 (1975) 100

57 H.Bock,G.Wagner and J.Kroner, Chem.Ber., 105 (1972) 3850

58 G.N.Dolenko,A.V.Zibarev,S.A.Krupoder,L.N.Mazalov,O.Ch.Poleshchuk, G.G.Furin,G.F.Khudorozhko and G.G.Yakobson, J.Fluor.Chem., 17 (1981) 1

59 J.J.Daly, J.Chem.Soc., (1964) 3799

60 C.P.Brock and J.A.Ibers, Acta Cryst., 29B (1973) 2426

61 A.W.Potts,H.J.Lempka,D.G.Streets and W.C.Price, Proc.Roy.Soc., 268A (1970) 59

62 I.A.Topol,A.V.Kondratenko,L.N.Mazalov,G.N.Dolenko and S.A.Chesny, Zh.Strukt.Khim., 22 (2) (1981) 22

63 O.I.Andreevskaya,S.A.Krupoder,G.N.Dolenko,G.G.Furin and G.G.Yakobson, Izv.Sib.Otd.Akad.Nauk SSSR,Ser.Khim., (1981) (3) 129

64 W.B.Perry,T.F.Schaaf and W.L.Jolly, J.Am.Chem.Soc., 97 (1975) 4899

65 S.Cradock and D.W.H.Rankin, J.Chem.Soc.,Faraday Trans.II, 68 (1972) 940

66 N.I.Al-Joboury and D.W.Turner, J.Chem.Soc., (1964) 4434

67 S.Cradock,E.A.W.Ebsworth and J.D.Murdoch, J.Chem.Soc., Faraday Trans.II, 68 (1972) 86

68 K.Katsumata,T.Iwai and K.Kimura, Bull.Chem.Soc.Japan, 46 (1973) 3391

69 A.P.Sadovsky,L.N.Mazalov,T.I.Guzhavina,G.K.Parygina and B.Ju.Chel'mer, Zh.Strukt.Khim., 14 (1973) 667

70 R.Larsson,A.Malek and B.Folkesson, Chem.Scripta, 16 (1981) 47

71 W.E.Morgan,W.J.Stec,R.G.Albridge and J.R.van Wazer, Inorg.Chem., 10 (1971) 926

72 E.Fluck and D.Weber, Pure Appl.Chem., 44 (1975) 373

73 Elecrton spectroscopy. Editor D.A.Shirley, Amsterdam, North Holland Publishers, 1972, p.681

74 A.T.Shuvaev, Izv.Akad.Nauk SSSR,Ser.Fiz., 25 (1961) 986

75 R.Kwart and K.King. d-Orbitals in Chemistry of Silicon, Phosphorus and Sulfur. Berlin,Springer-Verlag, 1977, p.4

76 Quantum-chemical methods of calculations. Editor Ju.A.Ustyny Moscow,Moscow state university Publishers,1980

77 G.Frenking,F.Marschner and H.Goetz, Phosphorus and Sulfur, 8 (1980) 337

78 Tables of Interatomic Distances and Configurations in Molecules and Ions. Editor L.E.Sutton, London,Burlington House Publishers, 1958

79 Molecular Structures and Dimensions. Editor O.Kennard e.a. N.V.A.Oosthoek's Uitgevers Mij.Utrecht, 1972,v. A1