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The Photoelectron Spectra and Molecular-orbital Characteristics of Covalent Aromatic Organoelemental Compounds

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The effects of the interaction of various heteroatoms (and heteroatomic fragments) with carbon π-electron systems in covalent organoelemental compounds are discussed in the review in terms of molecular orbital theory. Particular attention is devoted to the analysis of the structure of the molecular orbitals, determined from photoelectron spectroscopic data and quantum-chemical calculations within the framework of the simple Hückel molecular orbital method parametrised on their basis. It is shown that the parameters characterising the mixing of the orbitals in model compounds can be used to obtain the molecular-orbital characteristics and to interpret the spectroscopic properties and reactivities of complex heteroaromatic compounds.
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I. INTRODUCTION

The photoelectron spectra of aromatic organoelemental compounds, in which the heteroatoms are present in substituents or rings, together with the corresponding quantum-chemical calculations within the frameworth of the simple method make it possible to estimate the orbital mixing parameters of individual fragments in the molecules of these compounds and to obtain objective data for the molecular orbitals (MO), which determine the spectroscopic properties and reactivities of the compounds. Such information is important for the study of problems of chemical bonding within the framework of the molecular orbital theory and for the solution of practical problems—the establishment of new aromatic organoelemental systems[1], the synthesis of effective π-donors[2-5], the synthesis of phototropic compounds[6,7], etc. The interaction of the orbitals in aromatic organoelemental compounds has been analysed in reviews[8-11] concerned with the study of the influence of various substituents on the ionisation energies of substituted benzenes; the role of unoccupied *d* orbitals in certain organoelemental compounds has been discussed[12-16] and the ability of the atoms of heavy elements to form double bonds with carbon and with one another, etc. has been considered[17,18].

This review presents a survey of the quantitative estimates for the mixing of the orbitals of the π-electron systems of the carbon atoms and various non-carbon element-containing substituents and fragments incorporated in the rings. The estimates have been obtained from the analysis of the photoelectron spectra (PES) of the corresponding compounds and from quantum-chemical calculations within the framework of the simple method. We shall consider some aspects in greater detail.

In both non-empirical and semiempirical quantum-chemical calculations the orbitals of whole groups or molecular fragments rather than the atomic orbitals (AO) are used as the basis orbitals. In non-empirical calculations this is the SAMO method (simulated *ab initio* technique)[19,20], while in semiempirical calculations it is the group orbital method[20-24], which explains successfully the spectroscopic properties of many organic and organoelemental compounds[25-27]. Following the development of PES, the corresponding computational schemes have been applied effectively also in the simple quantum-chemical approximations[28,29]. Within the framework of such calculations, the molecular orbital is treated as a linear combination of bond orbitals in the LCBO-MO method[30-32], for example, while in the LCFO-MO scheme[33] it is treated as a linear combination of fragment orbitals. Despite the differences between the names and in certain specific problems, the essential features of the above schemes are identical; instead of atomic orbitals, "effective" orbitals, for example those of the individual molecular fragments, are considered in the basis set. Such schemes make calculations significantly less laborious and yield a particularly large amount of information in the study of the electronic and molecular structures of complex organoelemental compounds and in the first place compounds containing the elements of high Periods for which there are frequently no parameters in semiempirical methods.

In the solution of the Roothaan equations

$$\sum_{\mu=1}^{N} c_{\mu i}\,(H_{\mu\nu} - \varepsilon_i \delta_{\mu\nu}) = 0\,,$$

where μ and ν are the indices of the basis fragment orbitals, i is the index of the molecular orbital, $c_{\mu i}$ and ε_i are the coefficients and energies of the molecular orbitals, and $\delta_{\mu\nu} = 1$ (for $\mu = \nu$) or 0 (for $\mu \neq \nu$) is the Kronecker delta, by the simple method (Hückel's π-approximation), the influence of the interelectron interaction is taken into account implicitly in the parametrisation of the skeletal integrals $H_{\mu\mu}$ and $H_{\mu\nu}$. In particular, compared with the rigorous semiempirical methods in which the skeletal integrals are parametrised on the basis of atomic spectroscopic data, in the simple method the parametrisation based on molecular electronic spectra is apparently more useful: it has been suggested that $H_{\mu\mu}$ and $H_{\mu\nu}$ be estimated from photoelectron spectroscopic data for "model" compounds in which the corresponding μth and νth orbitals of the fragments are characterised by unoverlapped ionisation bands[28-31]. The parameters $H_{\mu\mu}$ and $H_{\mu\nu}$ found from the molecular spectra include to some extent the interelectronic effects (see below).

In terms of the π-approximation, only those fragment orbitals which have π-symmetry (or are close to it) relative to the molecular plane are included in the basis set of the simple calculation. For example, within the framework of the method of fragment orbitals, the integral H_S, corresponding to the $3p_\pi$ orbital of the sulphur atom in heterocyclic and heteroaromatic compounds, is estimated from the PES of compounds in which the sulphur atom is linked to two carbon atoms, in particular, the spectra of dimethyl sulphide[35] and not from the atomic spectrum of sulphur (where the ionisation potential of the $3p$ orbital is 13.32 eV[34]) and not from the PES of hydrogen sulphide (the ionisation potential of the b_1 orbital formed by the $3p_\pi$ orbital of sulphur is 10.47 eV[30]). One should bear in mind that in a compound of this kind (C_{2v} symmetry group) not only the $3p_\pi$(S) atomic orbital but also the (+)-combination of the $2p_\pi$ orbitals of two carbon atoms belong to type b_1. For this reason, the highest occupied molecular orbital ($2b_1$ orbital) of dimethyl sulphide is not identical with the p orbital of the sulphur atom, although it is generated predominantly by this orbital†:

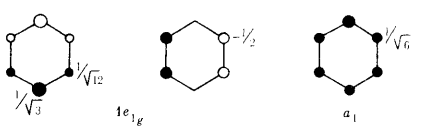
$$H_S = -I_{2b_1}^{SMe_2} = -8.67 \text{ eV}\,.$$

It is important to note that a further increase in the complexity of the molecule of the "model" compound alters little the parameter $H_{\mu\mu}$. For example, $H_S = -8.80$ eV, estimated in terms of the ionisation potential of the $3p_\pi$ orbitals of two sulphur atoms from the PES of 1,4-di(methylthio)benzene[30], differs only slightly from $H_S = -8.67$ eV found from the PES of dimethyl sulphide.

The parameters corresponding to the fragment orbitals localised predominantly at the atoms of other Group V–VII elements can be found analogously by simple quantum-chemical calculations in terms of the π-approximation; in this review these parameters are denoted respectively by H_O, H_{Se}, H_N, H_{Br}, etc.

The fragment orbitals involving the sp^3-hybridised orbitals of the atoms of Group IVA elements are taken into account in the calculations under consideration within the framework of the $\sigma-\pi$ conjugation scheme. The possibility of the overlap of the orbitals of the π- and σ-bonds located in a single plane but directed at an angle ϕ relative to one another has been discussed in detail in connection with the hyperconjugation model[36] and in another study[37] where this model was developed for organoelemental benzene derivatives. The integrals $H_{\mu\mu}$ corresponding to the σ(E–S) orbitals, are estimated from the first ionisation potentials of the compounds EMe_4: the orbitals of the four σ(E–C) bonds of the tetrahedral EC_4 fragment transform within the framework of the T_d symmetry group as $3t_2 + 1a_1$ and the triply degenerate t_2 orbital proves to be the highest occupied orbital. The corresponding diagonal matrix elements $H_{\mu\mu}$ will henceforth be designated by H_{EC}.

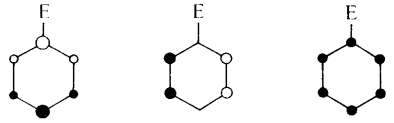
For the purpose of the present review, the π orbitals of aromatic hydrocarbons which can mix with the orbitals of the heteroatoms in heteroaromatic compounds are of special interest. The molecular orbitals of benzene have been studied in many investigations[38-45]. For example, according to the data of Dewar et al.[43] three π orbitals of benzene (the classification corresponds to the D_{6h} symmetry group) belong to types e_{1g} and a_{2u} and have the following coefficients (the filled circles correspond to positive coefficients and the open circles to negative coefficients; the size of the circles is proportional to the absolute magnitude of the coefficient):



It is known from the PES of benzene that the ionisation potential of the a_{2u} orbital is 12.23 eV[43] and the two degenerate e_{1g} orbitals have identical energies (their ionisation potential is 9.24 eV). Their degeneracy is removed after the introduction of a substituent E into the benzene molecule. In monosubstituted benzene derivatives C_6H_5E (C_{2v} symmetry) the benzene π orbitals transform as b_1, a_2, and b_1:

† According to a calculation by the extended Hückel method, the contribution of the $3p_\pi$ orbital of the sulphur atom is not less than 85% of the highest occupied molecular orbital (HOMO) of dimethyl sulphide.

they have come to be designated as the $\varphi_{\pi(sym)}$, $\varphi_{\pi(asym)}$, and φ_{π_1} orbitals respectively#:



$\varphi_{\pi(sym)}$, b_1 $\varphi_{\pi(asym)}$, a_2 φ_{π_1}, b_1

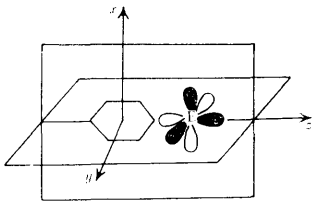
In conformity with the foregoing, in quantum-chemical calculations parametrised on the basis of PES data (simple method, π-approximation), the following diagonal elements $H_{\mu\mu}$ have been adopted for the benzene π orbitals as the fragment integrals:

$$H_{\pi(sym)} = H_{\pi(asym)} = -9.24 \text{ eV}; \; H_{\pi_1} = -12.23 \text{ eV}.$$

"Model" compounds in the PES of which an ionisation band corresponding to a linear combination of the μth and νth fragment orbitals is observed are used to estimate the non-diagonal integrals $H_{\mu\nu}$. By determining the corresponding ionisation potential I_i from the PES and setting $I_i = -\varepsilon_i$, one can find the parameter $H_{\mu\nu}$ from the secular equation

$$\begin{vmatrix} (H_\mu - \varepsilon_i) & H_{\mu\nu} \\ H_{\mu\nu} & (H_\nu - \varepsilon_i) \end{vmatrix} = 0 \; . \qquad (1)$$

The possibility of the involvement of particular fragment orbitals in the molecular orbitals is determined by their symmetry. For example, benzene derivatives PhE in which the substituents E contain the atoms of Group IV–VII elements (for example, $SiMe_3$, PMe_2, SMe, or Cl) have approximately C_{2v} symmetry. Under the influence of the symmetry operations, three π orbitals of the benzene ring and the p orbitals of the atom E transform as shown below:



C_{2v}	E	C_2^z	$\sigma_v^{(xz)}$	$\sigma_v^{(yz)}$	
φ_{π_1}	+1	−1	+1	−1	b_1
$\varphi_{\pi(sym)}$	+1	−1	+1	−1	b_1
$\varphi_{\pi(asym)}$	+1	+1	−1	−1	a_2
$\varphi_{p_z(E)}$	+1	+1	+1	+1	a_1
$\varphi_{p_y(E)}$	+1	−1	−1	+1	b_2
$\varphi_{p_x(E)}$	+1	−1	+1	−1	b_1

We shall assume that the HOMO of the compound PhE are produced as a result of the mixing of only the $\varphi_{\pi(sym)}$ orbital of benzene and the φ_{p_x} orbital of the heteroatom E. The parameter $H_{E\pi(sym)}$ characterising the degree of mixing of the above fragment orbitals, can then be found from Eqn.(1).

On the other hand, if account is taken of the fact that the HOMO of the substituted benzene is produced as a result of the mixing of not only the $\varphi_{p_\pi(E)}$ and the $\varphi_{\pi(sym)}$ orbitals but also the φ_{π_1} orbitals (all these orbitals belong to the same irreducible representation b_1 of the C_{2v} group), then the parameter $H_{E\pi(sym)}$ must be found from the solution of the third-order secular equation

$$\begin{vmatrix} (H_{\pi(sym)} - \varepsilon) & H_{E\pi(sym)} & 0 \\ H_{E\pi(sym)} & (H_E - \varepsilon) & H_{E\pi_1} \\ 0 & H_{E\pi_1} & (H_{\pi_1} - \varepsilon) \end{vmatrix} = 0 \; . \qquad (2)$$

The relations between the non-diagonal elements $H_{\mu\nu}$, characterising the interactions of the benzene π orbitals and the p_π orbital of the heteroatom E, are then employed:

$$H_{E\pi(sym)} \times \sqrt{3} = H_{E\pi(asym)} \times 2 = H_{E\pi_1} \times \sqrt{6} = H_{EC}. \qquad (3)$$

These are selected in accordance with the coefficients of the benzene π orbitals indicated above.

The inclusion of the φ_{π_1} orbital in the basis set alters only slightly $H_{E\pi(sym)}$. For example, the values of $H_{S\pi(sym)}$, obtained by the two methods described above and characterising the mixing of the fragment π orbital localised mainly at the sulphur atom with the benzene $\varphi_{\pi(sym)}$ orbital, are virtually identical: 0.84 ± 0.04 eV and 0.78 ± 0.06 eV respectively.

It must be specially emphasised that Eqn.(3) makes it possible to estimate the parameter H_{EC}, which characterises directly the interaction of the p_π orbital of the heteroatom E with the $2p_\pi$ orbital of the carbon atom.

The effects of the interelectronic interactions are taken into account in the values of the ionisation potentials found from the PES of "model" compounds and hence in the corresponding parameters $H_{\mu\mu}$ and $H_{\mu\nu}$. The quantum-chemical calculations based on this parametrisation procedure can therefore be carried out in terms of the scheme of the simple method without adjustment for self consistency.

Furthermore, the parameters $H_{\mu\mu}$ and $H_{\mu\nu}$, estimated from the ionisation potential obtained from the PES, include the reorganisation energy and the changes in the correlation and relativistic energies accompanying photoionisation. Thus the parametrisation of the quantum-chemical models, based on the PES data, removes to a large extent the limitations of the Koopmans theorem, which are evident in a comparison of the ionisation potentials I_i determined from the PES with the eigenenergies ε_i^{SCF} calculated in terms of the one-electron approximation[46,47]: $I_i = -\varepsilon_i^{SCF}$. This is probably why the quantum-chemical calculations employing the above parametrisation procedure are fairly reliable for the estimation of the electronic and molecular structures of complex organic and organoelemental compounds and are frequently comparable, as regards the amount of information they provide, with the results of much more cumbersome calculations by the self-consistent field (SCF) method.

In the subsequent Sections of this review, PES data for aromatic hydrocarbons and the corresponding aromatic organoelemental compounds will be discussed. The ionisation potentials of the compounds which it is proposed to regard as "model" compounds are compiled in Tables 1–3 and 6. It is noteworthy that the PES of organic compounds of certain elements have been discussed in a number of reviews[48–50]. However, the use of different quantum-chemical models by different investigators for the purpose of interpretation precludes the comparison on the basis of the data in the above reviews of the capacities of the orbitals of different elements for mixing with the π orbitals of carbon atoms. In order to discover the trends in the variation of the molecular-orbital parameters of the corresponding compounds as a function of the atomic number of the element, we present in the same Tables the results of our quantum-chemical analysis of the molecular orbital structures on the basis of the scheme proposed above. The integrals $H_{E\pi}$ and H_{EC} are compared as parameters in terms of which the degree of mixing of the orbitals is to be estimated.

This designation of the orbitals enumerated has been generally adopted for unsubstituted benzene and also in the analysis of the molecular-orbital structures of polysubstituted benzene derivatives and polycyclic compounds involving heteroatoms[30,32,43].

The mixing of the carbon π orbitals with the orbitals of the heteroatom not only in the "model" compounds, where the atoms of the elements are present as substituents, but also in cyclic compounds—π-donors, benzenes incorporating a non-carbon element in the ring, and the corresponding heterocycles—is analysed in this review.

II. THE π-ORBITALS OF BENZENE AND POLYCYCLIC AROMATIC HYDROCARBONS

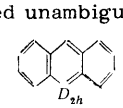
The molecular π orbitals of benzene have been thoroughly investigated and their structures were partly discussed above. The ionisation of degenerate $1e_{1g}$-π orbitals is observed at 9.24 eV, the ionisation of the highest-energy σ orbital is observed at 11.44 eV, and finally the ionisation of the lowest π orbital ($1a_{2u}$) is observed at 12.23 eV.[43] This assignment has been confirmed by the "perfluoro-effect"[44,45]: on passing from an unsaturated or aromatic compound to its perfluoroanalogue, the energies of the π orbitals change slightly, while the energies of the σ orbitals diminish appreciably, which can be seen from the ionisation potentials of hexafluorobenzene[45]: 10.12 eV (π_2, π_3); 12.73 eV (π_1); 14.02 eV (σ).

It has been shown for naphthalene[45] with the aid of the "perfluoro-effect" that a band in the PES beginning at 11 eV corresponds to the ionisation of its σ orbital; the bands in the region of lower energies refer to the ionisation of the π orbitals. This conclusion is in good agreement with the results of a non-empirical calculation according to which the four highest molecular orbitals of naphthalene are π orbitals and the fifth is a σ orbital. The same conclusion has been reached with the aid of calculations by the Hückel molecular orbital method using a parametrisation based on PES data[51-55]; the ionisation potentials (eV) and their assignments are listed below:



D_{2h} 8.12 ($1a_u$) 8.91 ($2b_{1u}$) 10.08 ($1b_{3g}$) 10.85 ($1b_{2g}$) 11.05 ($1b_{1u}$).

The dependence of the structure of the molecular orbitals of polycyclic aromatic hydrocarbons on the number of benzene rings has been investigated with the aid of various quantum-chemical methods and PES data[49,56-59]. It has been established that the energy of the σ orbital of benzene, corresponding to an ionisation energy of 11.44 eV in the PES, becomes 11.00 eV on passing to naphthalene and then does not change appreciably with increase of the number of condensed benzene rings. Therefore all the bands below 11.00 eV, for example in the PES of anthracene and phenanthrene, are assigned unambiguously to the ionisation of π orbitals:



D_{2h} 7.47 ($2b_{2g}$) 8.57 ($2b_{3g}$) 9.23 ($1a_u$) 10.26 ($1b_{2g}$) 10.40 ($2b_{1u}$).

The simple Hückel molecular orbital (HMO) method also yields satisfactory results for large polycyclic aromatic hydrocarbons: in particular, the vertical ionisation potentials I_i of polycyclic aromatic hydrocarbons determined from the PES correspond satisfactorily to the energies ε_i of the π orbitals calculated in units of β in terms of the HMO scheme:

$$I_i = -(\alpha_c + \varepsilon_i \beta_{cc}).$$

This makes it possible to determine the absolute values of the Coulombic integral α_C (within the framework of the simple method, the parameter α_C is identical with the diagonal element H_C) and the resonance integral β_{CC} (the integral β_{CC} is identical with the non-diagonal element H_{CC})[49]:

$$\alpha_c = H_c = -(6.55 \pm 0.34) \text{ eV},$$
$$\beta_{cc} = H_{cc} = -(2.73 \pm 0.33) \text{ eV}.$$

These values are convenient for simple quantum-chemical calculations of the energies of the π orbitals of aromatic hydrocarbons and their heterocyclic analogues[49,50,58,60].

III. CHARACTERISTIC FEATURES OF THE MIXING OF THE ORBITALS OF THE ATOMS OF GROUP II–VII ELEMENTS WITH THE π ORBITALS OF CARBON ATOMS

1. Halogen Atoms

The ionisation potentials of the *p* electrons of the halogen atoms are comparatively high. For example, the following values of *I* (eV) have been found from the PES of hydrogen halides: 16.03–16.06 for fluorine[61]; 12.74–12.82 for chlorine[62]; 11.64–11.98 for bromine[63]; 10.38–11.05 for iodine[62]. The ionisation energies of the unshared electrons of the halogens in halogenomethanes are somewhat lower and are listed in Table 1. This feature of the halogens is reflected in their higher electronegativity compared with carbon and hydrogen atoms[64].

Table 1. Estimation of the degrees of mixing of the *p* (halogen) and benzene π orbitals in the halogenobenzenes PhE.

E	*I*(E), eV	*I*(PhE), eV	$H_{E\pi(sym)}$, eV	Characteristics of the HOMO of PhE*					U.v. spectrum** (Ref.69)
				ε, eV	*ortho*	*meta*	*para*	c_E	
F	14.57 (Ref.52)	9.11 (b_1); 9.82 (a_2); 12.12 (b_1); 12.15 (Ref.67)	−0.84	−9.12	−0.311	0.269	0.566	0.150	210 (3.93); 261 (2.30)
Cl	11.28 (Ref.66)	9.06 (b_1); 9.69 (a_2); 11.32 (b_2); 11.70 (b_1) (Ref.67)	−0.63	−9.07	−0.313	0.256	0.550	0.270	210 (3.88); 257 (2.33)
Br	10.53; 10.86 (Ref.66)	8.99 (b_1); 9.67 (a_2); 10.61 (b_2); 11.18 (b_1) (Ref.68)	−0.62	−9.01	−0.314	0.239	0.530	0.367	204 (3.79); 254 (2.95)
I	9.54; 10.16 (Ref.66)	8.78 (b_1); 9.75 (a_2); 10.59; 11.70 (Ref.8)	−0.59	−8.80	−0.300	0.186	0.453	0.600	207 (3.86); 226 (4.12); 257 (2.85)

Note: *I*(E) are the ionisation potentials of the electrons of the *p*(E) orbital in the halogenomethanes MeE (according to PES data) and *I*(PhE) are the ionisation potentials of the halogenobenzenes (according to PES data).

* The characteristics of the HOMO of the halogenobenzenes (the energy ε and the coefficients c_μ) were obtained by ourselves as a result of calculation by the Hückel molecular orbital method with PES parametrisation (for the details of the calculation, see the Introduction): $H_C = -6.75$ eV; $H_{CC} = -2.5$ eV.[49].

** The positions of the absorption bands (in nm) are indicated (the logarithms of the molar extinction coefficients are shown in brackets).

Since the *p* orbitals of the fluorine atom ionise at the highest energy, the degree of their mixing with the more readily ionisable π orbitals of carbon in fluorobenzene molecules is not considerable, which constitutes the fundamental basis of the "perfluoro-effect" already mentioned, which

lowers significantly the energies of the σ orbitals and to a lesser extent those of the π orbitals. The *p* electrons of the chlorine, bromine, and iodine atoms ionise more readily, but this does not lead to more effective mixing of their orbitals with the π orbitals of the benzene ring, because the effectiveness of the mixing of the orbitals is determined not only by the difference between their energies and by their symmetry but also by their overlap[65]. Table 1 lists the ionisation potentials of the *p* electrons of the halogen atoms in halogenomethanes, the ionisation potentials of halogenobenzenes, and the positions of the intense long-wavelength absorption bands in the ultraviolet spectra of halogenobenzenes. It also lists the integrals $H_{E\pi(sym)}$ characterising the degree of mixing of the p_π orbitals of the halogens with the $\phi_{\pi(sym)}$ orbital of benzene.

The structure of the $\varphi_{\pi(asym)}$ orbital does not change but it has a lower energy, probably as a consequence of the inductive effect of the halogen.

In full agreement with numerous experimental data, it follows from a comparison of the coefficients of the HOMO of various halogenobenzenes that the halogen atoms are *ortho, para*-directing and that the directing effect is more marked for the fluorine atom. Comparison of the integrals $H_{E\pi}$ shows that the fluorine atoms are mixed to the greatest extent with the π orbitals of the benzene ring. However, in conformity with the coefficients c_E, the contribution of the unshared electrons of the halogen to the HOMO of the halogenobenzene increases in the sequence

$$F<Cl<Br<I .$$

The greatest bathochromic shifts are undergone by the absorption bands of benzene in the ultraviolet spectrum of fluorobenzene[69]: an intense long-wavelength absorption band is observed in the spectrum of fluorobenzene at 210 nm instead of 203 nm in the spectrum of benzene. In the ultraviolet spectrum of iodobenzene a new absorption band, compared with other halogenobenzenes, appears at 226 nm, which could be accounted for by the mixing of the $5p_x$ orbital of iodine and the π orbitals of benzene. However, the same band is observed also in the electronic spectrum of the iodide ion: apparently the absorption at 226 nm is a consequence of the local electronic transitions and is not related to the $p-\pi$ conjugation system. We may also note that the diphenyliodonium cation absorbs in the region of 226 nm[69,70] (the ultraviolet spectra of compounds in which the bromine and chlorine atoms are linked to two phenyl groups have been investigated[71-73]).

There exist also other estimates of the orbital interactions in halogenobenzenes[64,74-77]. In particular, the degree of mixing of the orbitals of the halogen atoms with the π orbitals of benzene has been estimated[75] in terms of a less rigorous criterion (compared with the integral $H_{E\pi}$ which we proposed), namely the splitting of the energies of the benzene b_1 and a_2 orbitals (the halogenobenzene and the splitting of the energies of these orbitals are indicated below in eV): fluorobenzene, 0.44; chlorobenzene, 0.57; bromobenzene, 0.64; iodobenzene, 0.71. According to this criterion, the 5*p* orbital of iodine is mixed with benzene orbitals to a greater extent than the 2*p*(F), 3*p*(Cl), and 4*p*(Br) orbitals[75].

2. Atoms of Oxygen Subgroup Elements

As in the fluorine subgroup, an increase of the atomic number of the element in the oxygen subgroup decreases its relative electronegativity. However, in aryl(alkyl) chalcogenides the influence of the steric structure on the conditions governing the mixing of the orbitals is significantly more appreciable (compared with halogenobenzenes). We shall examine as an example how the structure of compounds of the type R_2E varies for different E.

The valence angle in the hydrides H_2E diminishes on passing from oxygen to tellurium: 104.5° for O, 92.2° for S, 91.0° for Se, and 89.5° for Te.[78] In dimethyl chalcogenides Me_2E, the C–E–C valence angles are somewhat greater but the trend in their variation is the same: 111.5° for O,[78] 98.9° for S,[79] 98° for Se,[80] and 93° for Te.[81] The closeness of the C–E–C valence angle in the compounds R_2E to 90° can be used to characterise the deviation of the orbitals of the unshared electron pair from the *p* orbitals of the isolated atoms. Using this estimate, one can assume that in the series of dimethyl chalcogenides only the *p* orbitals of tellurium are hardly mixed with the orbitals of the methyl groups: the C–Te–C angle in dimethyl telluride differs insignificantly from 90°. The character of the unshared electrons of the chalcogen atoms in compounds of the type R_2E can be reliably determined within the framework of the molecular orbital method[30]. It has been found that, of the two pairs of unshared electrons formally not involved in the formation of bonds with the hydrogen atoms (for example in the water molecule), only one cannot mix with the *s* orbitals of the hydrogen atoms as a consequence of symmetry properties (b_1 for the C_{2v} symmetry group). The other orbital has the a_1 symmetry, i.e. the same as in the (+)-combination of the *s* orbitals of the hydrogen atoms and can mix with the latter.

In the dimethyl derivatives of the chalcogens Me_2E not only the $p_x(E)$ orbital but also certain combinations of the atomic orbitals of carbon can have the b_1 symmetry[35]. In these compounds the p_x orbital of the chalcogen is involved in the formation of the molecular orbital localised predominantly on the chalcogen: in the PES of dimethyl chalcogenides, the ionisation bands of the corresponding *p* orbitals of the chalcogens are comparatively narrow (although they are wider than in the PES of the hydrides[3]).

Evidently even wider possibilities for the mixing of the orbitals of the unshared electron pairs of the chalcogens with the orbitals of the substituents appear in the corresponding aromatic derivatives. This is probably why the C–E–C angle in compounds of the type PhEMe is even greater: 120° ± 2° for O,[82] 106° ± 2° for S,[83] 99.6° ± 2.5° for Se,[84] and 101° for Te[85]. The stereoelectronic factor exerts an even greater influence on the structure of the molecular orbitals of these compounds. For example, phenyl(alkyl) chalcogenides can exist in a conformation in which the alkyl group is oriented in the plane of the benzene ring and the p_x orbital exists under the most favourable conditions for mixing with the π orbitals of carbon (the dihedral angle $\phi = 0°$). For these compounds there is a possibility also of a different conformation which is sterically less hindered but is unfavourable from the standpoint of the energy of the $n-\pi$ conjugation. It is a perpendicular conformation in which the orbital of the unshared electrons is located in the plane of the benzene ring and can therefore mix only with the σ(CC) orbitals of the skeleton, while the E–C(H_3) bond is in a plane perpendicular to the benzene ring (the dihedral angle $\phi = 90°$).

The conformational properties of phenyl(alkyl) chalgogenides have been investigated by various methods. We shall note only some studies in which the PES method was used for this purpose. In a number of investigations intrinsic ionisation bands in the PES spectra of phenyl(methyl) chalcogenides were assigned to the "planar" ($\phi = 0°$) and "non-planar" ($\phi = 90°$) conformers[86-91]. On the other hand, the authors[85] assumed that the spectrum of telluroanisole reflects the planar conformation and the conformation with a dihedral angle $\phi \cong 60°$. However, the reliability of the

estimate based on PES data for non-planar conformations differing insignificantly in their energies has been questioned[92]. Overall, the data obtained show that the retention of free rotation of the substituents about the E–R bond in the compounds Ar–E–R does not prevent the mixing of the *p* orbitals of the chalcogens with the π orbitals of benzene.

The relative involvement of the *p*(E) orbitals and the π orbitals in the HOMO of anisole analogues is illustrated by the data in Table 2, which also lists the ionisation potentials of the unshared electron pairs of the chalcogens in the dimethyl chalcogenides Me_2E [they were used to estimate the energies of the p_π(E) orbitals which mix with the π orbitals] and the ionisation potentials of compounds of the type C_6H_5EMe. In order to estimate the integrals $H_{E\pi}$ within the framework of the LCFO-MO scheme, the first ionisation potentials of these compounds were employed.

Table 2. Estimation of the degrees of mixing of the *p* orbitals of Group VIA elements with the benzene π orbitals in the compounds PhEMe.

E	*I*(E), eV	*I*(PhEMe), eV	$H_{E\pi}$, eV	Characteristics of the HOMO of PhEMe*					U.v. spectrum** (Ref.97)
				ε, eV	c_{ortho}	c_{meta}	c_{para}	$c_{E(Me)}$	
O	10.04 (Ref.93)	8.21;9.17;10.76; 12.14;13.67; 15.37; [95] ***	−1.37	−8.33	0.38	−0.15	−0.47	−0.54	220 (3.89); 265 (3.13); 271 (3.30); 278 (3.27)
S	8.67 (Ref.94)	8.07;9.28;10.15 [86] ****	−0.84	−8.16	−0.30	0.10	0.36	0.77	254.5***** (3.99)
Se	8.40 (Ref.35)	7.99;8.29;9.24; 9.81;10.77 [90]	−0.72	−8.07	0.27	−0.08	−0.31	−0.84	250 (3.79); 271 (3.51)
Te	7.89 (Ref.35)	7.6–7.83;9.20; 10.27 [85]	−0.69	−7.70	0.24	−0.05	−0.26	−0.89	223 (3.99); 269 (3.69); 331 (2.84)

Note: *I*(E) are the ionisation potentials of the electrons of the *p*(E) orbital in the compounds Me_2E (according to PES data) and *I*(PhEMe) are the ionisation potentials of organoelemental derivatives of anisoles (according to PES data).

* The characteristics of the HOMO of the organoelemental derivatives of anisoles (the energies ε and the coefficients c_μ) were calculated by the Hückel molecular orbital method with PES parametrisation.

** The positions of the absorption bands (in nm) are indicated (the logarithms of the molar extinction coefficients are shown in brackets).

*** cf. Turner's data[96].

**** cf. the data of Bock et al.[42]

***** The absorption band of thioanisole at 200, 254, and 280 nm are indicated by Rodd[98].

Table 2 shows that in the series O, S, Se, Te the *p*(E) and π orbitals mix to the greatest extent for an element in a Second Period (as for the halogens). The most favourable combination of the above factors determining the degree of mixing of the orbitals is in fact encountered for oxygen. According to calculations by the Hückel molecular orbital method (PES parametrisation), the methoxy-group has the most powerful *ortho,para*-directing effect among other groups of the type EMe. With increase of the atomic number of the element, or with decrease of the ionisation potential of the electrons in the *p* orbital, and with the consequent increase of the difference between the energies of the interacting *p* and π(sym) orbitals, the contribution of the atomic orbitals of the chalcogen to the HOMO of the PhEMe molecule increases in the sequence

$$O<S<Se<Te.$$

On passing from anisole to thioanisole, selenoanisole, and telluroanisole, there is a bathochromic shift of the long-wavelength absorption in the ultraviolet spectra (Table 2). The maximum shift of the intense long-wavelength band is observed in the spectrum of thioanisole. These facts can be partly explained by the increased HOMO energy in the above series of compounds[97,99,100]. There is also a possibility of the involvement of unoccupied *d* orbitals for which the possibilities for mixing with the unoccupied π orbitals of benzene are in fact greatest in the case of the sulphur atom. The absorption bands at 223 and 231 nm, observed in the spectrum of telluroanisole, are apparently determined to a large extent by local effects.

We may also note that there exist other schemes for the parametrisation of the quantum-chemical calculations based on PES data[30,101–108]. In the method for the estimation of the parameters $H_{\mu\nu}$ adopted in this review the influence of the inductive effect of the substituent E on the energies of the benzene π orbitals and the difference between the inductive effects of the methyl and phenyl groups in the estimation of the energies of the atomic orbitals of the elements are not taken into account explicitly. In the parametrisation based on PES data for *p*-disubstituted benzenes, a correction has been made[30] for the alteration of the energy of the *n*(E) orbital as a consequence of the inductive influence of the benzene fragment but no account is taken of the difference between the sensitivities to the inductive effect of the benzene $\varphi\pi$(sym) and $\varphi\pi$(asym) orbitals.

Quantum-chemical studies in terms of the π-approximation, parametrised on the basis of PES data, have been used successfully[109–119] for the analysis of the molecular orbitals also of aromatic organoelemental compounds—monocyclic and polycyclic aromatic compounds containing heteroatoms in the ring. In particular, calculations in terms of the π-approximation were carried out using the parameters (eV)

$$\alpha_S = -9.4;\ \alpha_{Se} = -8.5;\ \alpha_C = -7.0;\ \beta_{CS} = -1.8;\ \beta_{CSe} = -1.5;\ \beta_{CC} = -3.0\ .$$

These made it possible to interpret reliably the PES of furan and its analogues[109,110]. For example, the $3p_\pi$ orbital of the sulphur atom in the thiophen molecule is fully conjugated with the π orbitals of carbon, which results in the formation of delocalised molecular orbitals, and on photoionisation it is not manifested by a separate band in the spectrum: the first two ionisation potentials of 8.9 and 9.5 eV have been attributed to the two highest π-electronic levels: $a_2(\pi)$ and $b_1(\pi)$ respectively. The replacement of the S atom by O, Se, and Te atoms affects only slightly the $a_2(\pi)$ level but alters significantly the energy of the $b_1(\pi)$ level. This type of dependence of the energies of the above molecular orbitals on the nature of the heteroatom can be understood by analysing their symmetries: the energy of the $a_2(\pi)$ molecular orbital, which has a nodal plane passing through the heteroatom, varies less than the energy of the $b_1(\pi)$ orbital to which the orbital of the heteroatom makes a considerable contribution[109,110]. The ionisation potentials (eV) of the a_2 and b_1 orbitals of compounds (I) are presented below:



(I)

	O	S	Se	Te
a_2	8.90	8.87	8.80	8.81
b_1	10.32	9.52	8.95	8.27

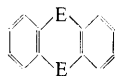
This contribution becomes a maximum for E = Te: the highest occupied orbital of tellurophen is a $b_1(\pi)$ orbital.

The character of the $p(E)-\pi$ mixing in tricyclic compounds is illustrated by the results of a study[119] in which the PES of dibenzofuran analogues were investigated and interpreted. The measured (PES) and calculated (Hückel molecular orbital method, PES parametrisation) ionisation potentials of, for example, dibenzoselenophen, are compared below:

I(exp.), eV	7.88	8.30	9.25	9.95	10.43	11.27	12.93
I(calc.), eV	8.07	8.51	9.25	9.81	10.07	11.47	12.58
Orbital	$5b_2$	$2a_2$	$4b_2$	$3b_2$	$2b_2$	$1a_2$	$1b_2$

Evidently the fragment π orbitals of the benzene nuclei and the p orbitals of the heteroatom are mixed in the molecule of this compound to the same extent as in the model compound: selenoanisole. An analogous conclusion applies also to other dibenzofuran analogues having planar molecules[120-123] and the maximum overlaps of the $p(E)$ and π orbitals. In the ultraviolet spectra of compounds of the dibenzofuran series, the greatest changes in the energies of the electronic transitions are observed on passing from dibenzofuran (absorption maxima at 249, 281, and 297 nm[124]) to dibenzothiophen (absorption maxima at 286, 313, and 323 nm[124]), while the spectra of dibenzoselenophen and dibenzotellurophen[125] are virtually identical with the spectrum of their thio-analogue.

In tricyclic compounds having the general structure

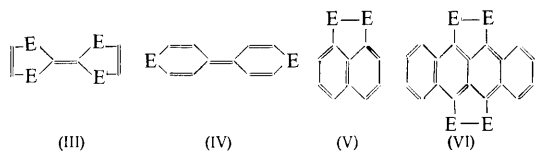


(II)

E = O, S, Se, Te

in the molecules of which the number of π electrons does not satisfy the Hückel rule for aromatic compounds, the p orbitals of the chalcogens and the carbon π orbitals are mixed less effectively. For example, the non-diagonal matrix element $H_{O\pi(asym)}$, found from the PES data for compound (II, E = O) is 0.94 eV, while 1.19 eV has been obtained from the PES of anisole. Although the molecule of dibenzo-*p*-dioxin is planar in the crystalline state[126], the discrepancies observed for compounds (II) between the measured and calculated ionisation potentials[127-129] can be due to the non-planarity of their molecules in the gas phase[130-132].

Among other compounds in which the chalcogen atoms are part of the composition of rings having more than six p electrons, mention should be made of derivatives of tetrathiafulvalene (III), dithiapyranylidene (IV), naphthalene (V), and tetracene (VI). The interest in the characteristics of the structure of the molecular orbitals of compounds (III)–(VI), in which E = O, S, Se, or Te, can be explained by the fact that the compounds exhibit electron-donating properties in highly conducting complexes with π acceptors[133-137]:



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

In particular the PES of tetrathio-, dithiodiseleno-, and tetraseleno-fulvalenes, (IIIa), (IIIb), and (IIIc), respectively have been investigated[135]. In the region of low ionisation energies (below 11 eV), all three compounds have virtually identical PES: the replacement of the S atom by Se does not invert the sequence of the molecular orbitals. It is significant that the energies of all the π orbitals, except the HOMO, increase somewhat on successive replacement of the sulphur atoms by selenium. On the other hand, the energy of the HOMO, which is the most delocalised orbital, decreases somewhat [the first ionisation potentials of the compounds (IIIa), (IIIb), and (IIIc) are respectively 6.70, 6.75, and 6.90 eV].

Interesting results have been obtained by the LCFO-MO method in the analysis of the orbital interactions in naphthalene 1,8-disulphide (V).[136] The occupied molecular π orbitals of the compound are produced from the corresponding orbitals of two fragments—the naphthalene molecule and the disulphide bridge. The following molecular orbitals were taken into account for the naphthalene fragment (symmetry group approximately C_{2v})[45]: a_2 (−8.13 eV); b_1 (−8.88 eV); b_1 (−10.01 eV); a_2 (−11.37 eV); b_1 (−13.0 eV). The interaction between the p_π orbitals of two neighbouring sulphur atoms leads to two new energy levels [−8.1 (a_2) and −10.1 (b_1) eV] to which correspond wave function in the form of linear $p(-)$ and $p(+)$ combinations[138,139]. The determination of the energies of the molecular orbitals of naphthalene 1,8-disulphide reduces to the solution of two secular equations set up respectively for the a_2 and b_1 orbitals. The diagonal matrix elements $H_{\mu\mu}$ are set equal to the energies of the basis fragment orbitals (FO) and the non-diagonal matrix elements are found from the relation

$$H_{\mu\nu} = \sqrt{2} \cdot C_\mu \beta_{CS},$$

where C_μ is the coefficient of the molecular orbital of naphthalene at the site of the addition of the disulphide bridge (for the 1- and 8-positions, the values of C_μ are identical and for the four occupied molecular orbitals enumerated above they amount to 0.425, 0, 0.263, and 0.301 respectively) and β_{CS} is the integral characterising the interaction of the $2p(C)$ and $3p(S)$ orbitals; $\beta_{CS} = -1.8$ eV has been adopted[140]. The corresponding secular equations in the case under consideration have the following form:

$$\begin{vmatrix} (-8.13-\varepsilon) & 0.60\beta_{CS} & 0 \\ 0.60\beta_{CS} & (-8.10-\varepsilon) & 0.37\beta_{CS} \\ 0 & 0.37\beta_{CS} & (-11.37-\varepsilon) \end{vmatrix} = 0;$$

$$\begin{vmatrix} (-10.01-\varepsilon) & 0.57\beta_{CS} & 0 \\ 0.57\beta_{CS} & (-10.1-\varepsilon) & 0.43\beta_{CS} \\ 0 & 0.43\beta_{CS} & (-13.80-\varepsilon) \end{vmatrix} = 0.$$

Calculated data agree very well with experimental results.

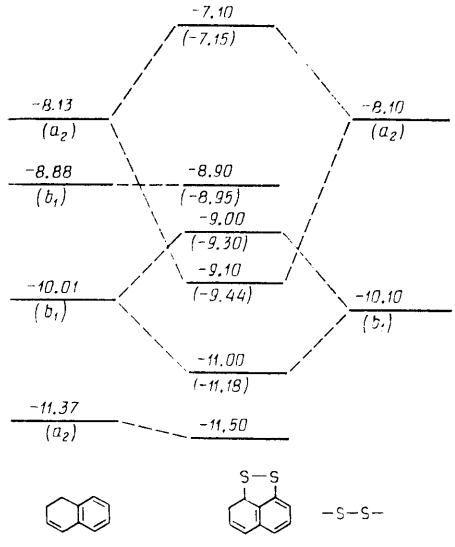


Figure 1. Schematic illustration of the formation of the π orbitals of 1,8-naphthylene disulphide[136] (the energies are indicated in electron-volts).

Fig. 1 illustrates a qualitative diagram describing the distribution of the π orbitals with respect of energy in the naphthalene 1,8-disulphide molecule (the estimated molecular orbital energies are indicated: the values based on PES data in brackets and the calculated values without brackets).

In conclusion of the discussion of the characteristics of the formation of the molecular orbitals from the fragment p(E) and π orbitals in compounds of Group VIA elements, we may note that, although the degree of mixing of the fragment orbitals decreases in the sequence O > S > Se > Te, selenium compounds and in certain cases also tellurium compounds have been found to be the most promising π donors in the corresponding complexes of organic metals[141,142].

3. The Atoms of Nitrogen-Subgroup Elements

In contrast to dimethyl chalcogenides Me_2E, in the series of compounds Me_3E (where E = N, P, As, or Sb) the increase of the atomic number and the decrease of the electronegativity of the element E never lead to a decrease of the ionisation potentials of its unshared electrons: the ionisation potentials of trimethylamine, trimethylphosphine, and trimethylarsine are almost identical (a slight increase is actually observed on passing from nitrogen to arsenic)[143]. The ionisation potentials of the unshared electron pairs of the heteroatoms in the hydrides H_3E differ to a greater extent[144]; The corresponding data are presented in Table 3.

Table 3. *Estimation of the degrees of mixing of the n orbitals of Group VA elements with the benzene π orbitals in the compounds* $PhEMe_2$.

E	I(E), eV* (Ref.143)	I(PhEMe2), eV	H_{Em}, eV	Characteristics of the HOMO of PhEMe2*					U.v. spectrum** (Ref.149)
				ε, eV	c_{ortho}	c_{meta}	c_{para}	c_E(Me2)	
N	8.50	7.6;9.2;10.0 [146]	−1.21	−7.82	−0.36	0.08	0.39	0.72	251 (4.15); 299 (3.31)
P	8.60	8.45 (*n*); 9.2 (a_2+b_1) [146]	−0.34	−8.47	−0.18	0.08	0.23	0.91	251 (3.54)
As	8.65	8.67 (*n*); 9.31 (a_2+b_1); 10.7—11.0 [148]	0.0	—	—	—	—	—	241.5 (3.83)
Sb	8.48	—		—	—	—	—	—	250 (2.57)

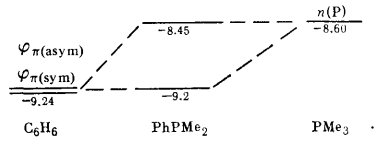
Note: I(E) are the ionisation potentials of the electrons in the n(E) orbital in the compounds Me_2E (according to PES data) and I($PhEMe_2$) are the ionisation potentials of the analogues of *N,N*-dimethylaniline (according to PES data).

* The characteristics of the HOMO of the compounds $PhEMe_2$ (the energies ε and the coefficients c_μ) were calculated by the Hückel molecular orbital method with PES parametrisation (for the details of the calculations, see the Introduction).

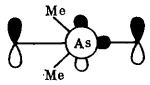
** The positions of the absorption bands (in nm) are indicated (the logarithms of the molar extinction coefficients are shown in brackets).

In analysing this feature of compounds of Group VA elements, one must bear in mind the variation of the geometry, in particular in the series of compounds Me_3E and the corresponding variation of the hybridisation of the orbital of the unshared electrons of the heteroatom: for example, the C—E—C angle decreases from 108° for NMe_3 to 99° for PMe_3 and 96° for $SbMe_3$. According to Walsh[145], the increase of the deviation from the planar structure on passing from nitrogen to antimony corresponds to an appreciable alteration of the hybridisation of the orbital of the unshared electrons, to an increase of its *s* character, and to the corresponding decrease of its energy. Such hybrid orbitals of the unshared electrons of Group V elements would apparently be more correctly designated by the letter *n* rather than *p*.

It appears that the mixing of the *n* orbital with the π orbitals of the corresponding benzene derivatives $PhEMe_2$ depends primarily on the degree of hybridisation of the *n* orbital[146,147]. In contrast to *N,N*-dimethylaniline, in the molecule of which the *n* orbitals of nitrogen and the orbitals of carbon are actively mixed, in *P,P*-dimethylphenylphosphine the degree of $n(P)-\pi$ mixing is much lower[146] (Table 3):



The conformations and PES of dimethylvinyl- and dimethylphenyl-arsines have been investigated[148]. In these compounds the n(As) and π orbitals are not mixed; the first ionisation potentials of trimethylarsine and dimethylphenylarsine are almost identical, amounting to 8.65 and 8.67 eV respectively. It is of interest to note that the calculation by the CNDO/2 method for dimethylphenylarsine showed that the optimum conformation is one in which the *n* orbital of the arsenic atom, the bisector of the Me—As—Me angle, and the benzene ring are located in a single plane:



This conclusion is not unexpected: the same conformation had been observed earlier in solution for dialkyl(*p*-tolyl)-phosphines[150]. On the other hand, consistent with the assumption made, the *N,N*-dimethylaniline molecule has a conformation favourable for the $n(N)-\pi$ conjugation: the $PhNC_2$ fragment is almost planar—the average C—N—C angle is 116°.[151] In this connection we may note that the effect of the $n(P)-\pi$ conjugation in the series of compounds of tricoordinate phosphorus and its analogues have been investigated in detail also by other methods, in particular by potentiometric titration[152].

Table 4. The ionisation potentials (I, eV) of the compounds Ph_3E according to PES data[154].

E	I_1	I_2	I_3	I_4
N	7.00	8.81	9.25	10.29
P	7.85	9.02	9.18	9.68
As	8.03	—	9.10	9.58
Sb	8.08	—	9.06	—

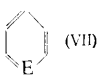
The formation of the molecular orbitals of triphenylamine and its analogues of the type Ph_3E has been investigated[153,154]. Table 4 lists the vertical ionisation potentials of Ph_3E, which lie below 11 eV.[154] The ionisation potentials at 9 eV (I_2 and I_3) were attributed to orbitals localised preferentially in the

benzene rings; the ionisation potentials I_1 and I_4 were assigned to the orbitals formed by the mixing of the benzene π orbitals and the orbitals of the unshared electrons of the heteroatom. The maximum mixing of the n(E) and carbon π orbitals is observed in triphenylamine: the PES of this compound does not reveal the ionisation of isolated n(N) and π orbitals. The first band in the PES, characterising the n(E)–π mixing, becomes narrower on passing from N to P and further to As and Sb.[153] As in the series of compounds $PhEMe_2$, in the present series of compounds the degree of n(E)–π mixing diminishes sharply on passing from N to P and falls still further on transition to As and Sb:

$$N \gg P > As > Sb .$$

The PES data for p-disubstituted benzenes described by the formula p-$Me_2EC_6H_4EMe_2$ are fully consistent with the conclusion that the degrees of n(E)–π mixing in the nitrogen and phosphorus compounds are significantly different[147].

However, it must be emphasised yet again that the weak capacity of the n orbital of the tricoordinate phosphorus atom (and also arsenic and antimony atoms) for mixing with the π orbitals is caused by the characteristics of its hybridisation. The alternative explanation of the above phenomenon, based on geometrical causes [the difference between the effective dimensions of the 3p(P) and 2p(C) orbitals, the greater E–C bond length compared with the N–C bond length, etc.], is hardly likely to be valid, because heteroaromatic compounds with dicoordinate atoms of Group VA elements, up to bismuthabenzene, are known:



(VII)

E=N, P, As, Sb, Bi .

The steric and electronic structures of organoelemental derivatives of benzene of type (VII) have been studied in detail and discussed in a number of reviews[48,155]. In the present review we shall confine ourselves to the principal conclusions reached in the investigations concerning the comparative estimates of the degrees of mixing of orbitals of different elements.

The molecules of compounds (VII) are planar and their bond lengths are characteristic of aromatic compounds. For example, according to the data of Bart and Dely[156], the phosphorus–carbon bond length in 2,6-dimethyl-4-phenylphosphabenzene is 1.74 Å, while the length of the P=C double bond in the $Ph_3P{=}CH_2$ is 1.65 Å and that of the P–C single bond in trimethylphosphine is 1.87 Å. The carbon–nitrogen, carbon–arsenic, and carbon–antimony bond lengths in the corresponding organoelemental derivative of benzene are 1.37 Å,[157] 1.85 Å,[158] and 2.05 Å.[159]

The principal spectroscopic characteristics of the organoelemental derivatives of benzene (VII) are listed in Table 5. The structure of the occupied molecular orbitals in these compounds can be naturally accounted for within the framework of the simple molecular orbital perturbation scheme (theory)[160]: the changes in the energy levels of the benzene π orbitals are determined by the coefficients of these orbitals referring to the position of the heteroatom. In conformity with the squares of these coefficients for the π orbitals of benzene (0.33 for $2b_1$, 0 for a_2, and 0.17 for $1b_1$), the greatest changes following the introduction of the heteroatom are undergone by the ionisation potential of the φ_π(sym) orbital (the $2b_1$ orbital); the energy of the π_1 orbital (the $1b_1$ orbital) changes less and finally the energy of the φ_π φ_π(asym) orbital (the a_2 orbital) hardly changes when the CH fragment is replaced by a heteroatom. We may note that there are linear relations between the ionisation potentials of the π orbitals of compounds (VII) and the ionisation potentials I_E of the p orbitals of the elements[160]:

$$I_{(2b_1)} = (5.24 + 0.36I_E), \text{ eV} \quad (r = 0.9998) ;$$
$$I_{(1b_1)} = (10.25 + 0.16I_E), \text{ eV} \quad (r = 0.9908).$$

(The values of I_E are 14.53 eV for N, 11.0 eV for P, 9.81 eV for As, and 8.64 eV for Sb.)

Table 5. The spectroscopic characteristics of organoelemental derivatives of benzenes PhE (E is a Group VA element).

E	I(PhE)*, eV (Ref.160)	U.v. spectrum** (Refs. 17, 161)
N	9.7–9.8 ($11a_1$, σ/n; $1a_2$, π), 10.5 ($2b_1$, π); 12.5 ($7b_2$, σ); 12.6 ($1b_1$, π)	175 (4.90); 192 (3.80); 250 (3.30) 270 (2.65)
P	9.2 ($3b_1$, π); 9.8–10.0 ($1a_2$, π; $13a_1$, σ/n); 11.5 ($8b_2$, σ); 12.1 ($2b_1$, π)	213 (4.28); 246 (3.93); 290 sm. (2.40)
As	8.8 ($5b_1$, π); 9.6–9.9 ($2a_2$, π; $17a_1$, σ/n); 11.0 ($10b_2\sigma$); 11.8 ($4b_1$, π)	219 (4.18); 268 (4.04); 305 sm. (2.54)
Sb	8.3 ($7b_1$, π); 9.4–9.6 ($3a_2$, π; $21a_1$, σ/π); 10.4 ($12b_2$, σ); 11.7 ($6b_1$, π)	236; 312

* The ionisation potentials of organoelemental derivatives of benzene (according to PES data).
** The positions of the absorption bands (in nm) are indicated (the logarithms of the molar extinction coefficients are shown in brackets); the solvent was cyclohexane.

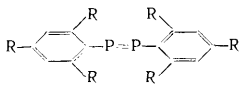
The analysis of the structure of the occupied molecular orbitals of the organoelemental derivatives of benzene (VII) described above has been justified[160] with the aid of an *ab initio* calculation for phosphabenzene whereby it was found that none of the occupied molecular orbitals of this compound contains an appreciable contribution of the unoccupied 3d(P) orbitals (there exists also a different view concerning the role of these orbitals in the formation of the molecular orbitals of phosphabenzene[162]).

It is of interest to compare the fact of the active involvement of the p(E) orbitals in the formation of the π-type molecular orbitals of organoelemental benzene derivatives with data concerning the character of the orbitals of the unshared electrons of the heteroatoms in these heterocycles: the ionisation of the unshared electrons is manifested in the PES of both the hydrides H_3E and organoelemental benzene derivatives in the region of 10 eV, but the corresponding bands in the spectrum are overlapped by the band due to the ionisation of the benzene π orbitals[160,163–165]. The ionisation of the unshared electrons of the sp^2-hybridised phosphorus atom was first observed in the form of an individual band by Schäfer et al.[164]; the band half-width in the PES of 2-phosphanaphthalene proved to be only 20% smaller than the half-width of the band due to the ionisation of the unshared electrons of the sp^3-hybridised phosphorus atom. The n orbital of the phosphorus atom, located in the plane of the carbon fragment in the molecules of aromatic phosphorus compounds (phosphabenzene, phosphanaphthalene, and phospha-anthracene), is apparently mixed with the σ(CC) orbitals.

The capacity of the 3p(P) orbitals for appreciable overlapping with the 2p(C) orbitals had been observed earlier in linear compounds, in particular in coloured compounds of the type of cyanines and triarylmethanes[166–169]: X-ray diffraction studies showed, for example, that the phosphorus–carbon bond length in phosphamethinecyanines is

1.76 Å[168,169], i.e. is virtually the same as in phosphabenzene (1.74 Å).

The geometrical parameters of the *p* orbitals of the elements of high Periods do not prevent their overlap with both the π orbitals of the sp^2-hybridised carbon atom and with the *p*(E) orbital of another E atom. Bis(2,4,6-tri-t-butylphenyl)diphosphene, the first stable compound with a double bond between phosphorus atoms, has been recently isolated and characterised[170] (cf. the earlier communications[171-173]):



(VIII)

R = t-Bu .

The molecule of the diphosphene (VIII) is planar and the P=P bond length is 2.034 Å; its ultraviolet spectrum [284 (ε = 15660), 340 (ε = 7690), and 460 (ε = 1360)] resembles very closely that of its *N*-analogue—bis(2,4,6-tri-t-butylphenyl)diazene[174].

4. The Atoms of Carbon Subgroup Elements

We shall now discuss the behaviour of the benzene π orbitals under the influence of substituents incorporating atoms of the Group IVA elements. In the sp^3 valence state these elements form bonds assuming tetrahedral directions and have comparatively low ionisation potentials. In the corresponding non-planar compounds the σ and π orbitals of the individual fragments are therefore capable of mixing, although, for example, in compounds having the general structure $PhEMe_3$, the perturbation of the benzene π orbitals is slight: the first ionisation potential decreases by only 0.24 eV on passing from benzene to trimethylphenylsilane.

The interaction of the π orbitals of the benzene ring with the orbitals of the σ(E—C) bonds in the compound $PhEMe_3$ has been discussed in detail in many communications; certain questions concerning this problem were considered above (in the introduction).

In the series of compounds $PhEMe_3$, one is dealing with the possibility of the mixing of the benzene $\varphi_{\pi(sym)}$ and σ(E—Me) orbitals[37]. The ionisation potential of the electrons of the σ(E—C) orbitals in the series of compounds Me_4E varies in parallel with the variation of the electronegativity of the element E[175]. However, one should note that the first ionisation potentials of the compounds $PhEMe_3$ vary only slightly: the degree of mixing of the σ(E—C) and π orbitals in the phenyl derivatives of the elements of the carbon subgroup as well as the degree of mixing of the *n*(E) and π orbitals in the corresponding compounds of Group V—VII elements decrease with increasing atomic number of the element:

$$C > Si > Ge > Sn .$$

The corresponding data, including the results of quantum-chemical calculations for the compounds $PhEMe_3$ in terms of the π-approximation (parametrisation based on PES), are presented in Table 6.

It is noteworthy that the longest-wavelength absorption is observed in the ultraviolet spectra of phenylsilanes. The maximum shift of the absorption band has been observed in

Table 6. Estimation of the degrees of mixing of the σ(E—C) and σ(C—E) orbitals with the benzene π orbitals in the compounds $PhCH_2EMe_3$ and $PhEMe_3$.

E	*I*(E-C), eV	Ionisation potential*, eV (Ref.43)	*H*(EC), eV	Characteristics of HOMO**					U.v. spectrum**** (Ref.177)
				ε, eV	c_{ortho}	c_{meta}	c_{para}	c(EC)***	
				$PhEMe_3$					
C (IX)	11.4	8.83 (π_2); 9.31 (π_3); 10.92; 11.39 (σ (CC)); 12.11 (π_1); 12.72; 12.93; 14.93	−1.03	−8.85	−0.34	0.22	0.53	0.36	208 (3.93); 258 (2.30)
Si (X)	10.5	9.00 (π_2); 9.26 (π_3); 10.48—10.60 (σ (SiC); 11.56; 11.91 (π_2) [176]	−0.60	−9.01	−0.31	0.24	0.53	0.37	211 (4.03); 260 (2.48)
Ge (XI)	10.2	9.00 (π_2); 9.25 (π_3); 9.98—10.30 (σ (GeC); 11.63 (σ (CC)); 11.97 (π_1); 12.80; 13.91	−0.54	−9.01	−0.31	0.23	0.52	0.41	208 (4.08); 258 (2.30)
Sn (XII)	9.7	8.94 (π_2); 9.29 (π_3); 9.71—10.02 (σ (SnC); 11.58 (σ (CC); 12.02 (π_1); 12.72; 13.87	−0.48	−8.95	−0.30	0.21	0.48	0.53	209 (4.09); 252 (2.78)
				$PhCH_2EMe_3$					
C (XIII)	11.4	8.77 (π_2); 9.13 (π_3); 10.73; 11.41 (σ (CC)); 12.10 (π_1); 12.49; 13.81	−1.21	−8.73	−0.36	0.21	0.52	0.39	211 (4.67); 259 (2.24)
Si (XIV)	10.5	8.42 (π_2); 9.08 (π_3); 10.53 (σ (C Si); 11.40 (σ (CC)); 11.98 (π_1); 12.78; 13.55	−1.33	−8.48	−0.37	0.17	0.49	0.49	222 (3.94); 267 (2.63)
Ge (XV)	10.2	8.40 (π_2); 9.12 (π_3); 10.41 (σ (CGe)); 11.43 (σ (CC)); 12.01 (π_1); 12.92; 13.67	−1.39	−8.36	−0.38	0.15	0.48	0.52	225 (3.86); 269 (2.53)
Sn (XVI)	9.7	8.21 (π_2); 9.21 (π_3); 9.90—10.32 (σ (CSn); 11.42 (σ (CC)); 11.99 (π_1); 12.83,13.25	−1.35	−8.24	−0.38	0.14	0.46	0.58	236 (3.74); 272 (2.69)

Note: *I*(E—C) are the ionisation potentials of the σ(E—C) orbitals in the compounds Me_4E (according to PES data).

* The ionisation potentials of the compounds $PhEMe_3$ and $PhCH_2EMe_3$ are indicated (according to PES data).

** The characteristics of the HOMO of the compounds $PhEMe_3$ and $PhCH_2EMe_3$ (the energies ε and the coefficient c_μ were obtained by ourselves from calculations by the Hückel molecular orbital method with PES parametrisation (see the Introduction for the details of the calculations).

*** The coefficient c(CE) are indicated for the compounds $PhCH_2EMe_3$.

**** The positions of the absorption bands in nm are indicated (the logarithms of the molar extinction coefficients are given in brackets).

the ultraviolet spectrum of *p*-bis(trimethylsilyl)benzene [absorption bands at 226 and 270 nm compared with the bands at 214 and 263 nm in the ultraviolet spectrum of *p*-bis(t-butyl)benzene].[178] This feature is probably due to the contribution of the unoccupied 3*d* orbitals of silicon to the unoccupied molecular orbitals of phenylsilanes, which reduces the energies of these molecular orbitals. The molecular orbital perturbation theory[43] and the CNDO/2 method (both with and without the inclusion of the 3*d* orbitals in the basis set)[179] have been used for quantitative estimates of the contributions of the 3*d*(Si) orbitals.

Since the unoccupied d_{xz} orbitals of silicon have b_1 symmetry (relative to the C_{2v} group, they can be mixed also with the occupied σ and π orbitals of benzene having the same symmetry, which decreases the energy levels of the corresponding HOMO and hence also the absolute value of the integral $H_{\sigma\pi}$ characterising the degree of σ–π mixing in the compounds $PhEMe_3$. Furthermore, the low degree of mixing of the π and σ(E–C) orbitals in the series of compounds (X)–(XII) can probably be explained also by the fact that the C_{ar}–E(Me) bond length increases on passing from Si to Sn, which hinders the mixing.

A more objective estimate of the capacity of various σ(C–E) orbitals for mixing is possible on comparing the corresponding spectroscopic characteristics of the benzyl derivatives $PhCH_2EMe_3$: in these compounds the C_{ar}–C(E) bond length is independent of E and the capacity for overlap of the *d* orbitals of the element with the benzene π orbitals is also significantly reduced. The ionisation potentials measured by the PES method[43,180], the results of quantum-chemical estimations, and the positions of the long-wavelength absorption bands in the ultraviolet spectra of the compounds $PhCH_2EMe_3$ are also presented in Table 6. As was to be expected, the degree of mixing of the σ(C–E) and π orbitals in these compounds is determined mainly by the difference between their energies and is therefore a maximum for the σ(C–Ge) and σ(C–Sn) orbitals.

The results presented in Table 6 agree well with the experimental data[37] and with the estimates[180] of other workers. Here it is appropriate to mention the results obtained when account is taken of contributions of different kinds to the observed changes in the energies of the highest occupied molecular orbitals. In particular, the results of such analysis have been obtained for the phenyl and benzyl derivatives of Group IVA elements $PhEMe_3$ and $PhCH_2EMe_3$.[43] Within the framework of molecular orbital perturbation theory, the changes in the energies of the benzene π_1 and $\pi_{2(sym)}$ orbitals δE_{π_1} and δE_{π_2} can be represented as the sums of the inductive ($q_{\mu i}.\delta W_i$) and hyperconjugation ($\beta^2 q_{\mu i}\Delta E^{-1}$) contributions:

$$\delta E_{\pi_1} = (1/6)\delta W + (1/6)\beta^2 (E_{\pi_1} - E_\sigma)^{-1},$$
$$\delta E_{\pi_2} = (1/3)\delta W + (1/3)\beta^2 (E_{\pi_2} - E_\sigma)^{-1},$$

while the change in the energy of the σ(E–C) orbital is defined by the formula

$$\delta E_\sigma = (1/3)\beta^2 (E_\sigma - E_{\pi_2})^{-1} + (1/6)\beta^2 (E_\sigma - E_{\pi_1})^{-1}.$$

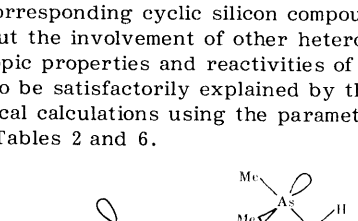
In these expressions E_σ, E_{π_1}, and E_{π_2} are the energies of the corresponding unperturbed orbitals, $q_{\mu i}$ is the electron density of the φ_μ orbital at the *i*th centre, δW_i is the change of the effective ionisation potential of the *i*th carbon atom as a consequence of the inductive effect of the substituent, and β is the resonance integral between the 2*p*(C) orbital of the *i*th atom and the orbital of the substituent. The electron-accepting influence of the unoccupied *d* orbitals has been estimated by comparing the calculated and experimental estimates of δE_{π_2}. Table 7 summarises the results obtained. The determination of the contributions of the individual components enumerated in Table 7 is based on the experimental estimates of δE_{π_1}, δE_{π_2}, and δE_σ. The accuracy of such estimates is low and they must be regarded as extremely approximate; in particular, unstructured bands in the PES correspond to the ionisation of the σ orbitals. This is possibly why the hyperconjugation contributions by the carbon–element bonds in the benzyl compounds have been found to be clearly too low: they proved to be smaller even than the inductive contributions and also the corresponding contributions in compounds of the type $PhEMe_3$. Such results conflict with the estimates of other authors and the experimental data[37,180]. The effects of the mixing of the σ and π orbitals have also been investigated for the corresponding allyl compounds[180]. It is of interest that here the authors concluded that the resonance integrals β for the π and σ(C–E) orbitals are constant (for different E).

Table 7. Analysis of the causes of the changes in the orbital energies in the compounds $PhEMe_3$ and $PhCH_2EMe_3$ (according to the data of Dewar et al.[43]).

Compound	Contributions to δE_{π_2}, eV				Contributions to δE_{π_1}, eV		
	inductive	hyperconjugation	p_π–d_π	sum	inductive	hyperconjugation	sum
(X)	0.78	0.51	–1.09	0.20	0.39	–0.12	0.27
(XI)	0.64	0.38	–0.82	0.20	0.32	–0.06	0.26
(XII)	0.48	0.34	–0.51	0.31	0.24	–0.03	0.21
(XIV)	0.30	0.10* (0.7)	—	0.40	0.15	–0.05	0.10
(XV)	0.28	0.14* (0.9)	—	0.42	0.14	–0.07	0.07
(XVI)	0.38	0.23* (1.0)	—	0.61	0.19	–0.10	0.09

* Estimates of the hyperconjugation effect based on the data of Schweig et al.[180] are presented in brackets for comparison.

Among other types of organic compounds of Group IVA elements, in which the σ and π orbitals are mixed, one should mention arylpolysilanes[181–183]. Estimates of the degree of σ(Si–Si)–π mixing in their molecules have been obtained from PES data and the absorption spectra of charge-transfer complexes and the influence of the stereoelectronic factor has been revised[184]. The σ(Si–C) and π orbitals are also mixed in the corresponding cyclic silicon compounds both with and without the involvement of other heteroatoms[176,185]. The spectroscopic properties and reactivities of these compounds can also be satisfactorily explained by the results of quantum-chemical calculations using the parameters enumerated above in Tables 2 and 6.



The σ–π mixing is undoubtedly not a specific feature of organic compounds of Group IVA elements. For example, it also occurs in allyl sulphides[186]. The dependence of the degree of mixing of the σ(C–As) and π orbitals on the conformation has been studied[148]. It has been found that these orbitals are not mixed in benzyldimethylarsine, but their contribution to the HOMO of allyldimethylarsine, which has a different conformation, is extremely significant.

As for the atoms of Group VA elements, the 3*p* orbital of the silicon atom can be mixed with the carbon π orbitals to form molecular orbitals of the corresponding aromatic compounds. Among such compounds, mention should be made in the first place of silabenzene and silatoluene—compounds in which the silicon atom is in a tricoordinate state and which exhibit properties characteristic of aromatic compounds. Owing to their exceptionally high reactivity, it was for a long time not only impossible to isolate silabenzene and silatoluene in a pure state and to investigate them using appropriate chemical reactions but it was actually not possible to detect them by employing "trapping" reactions[17]. However, theoretical calculation showed that silabenzene should be thermodynamically very stable. In particular, it followed from the MINDO/3 calculation that the C—Si bond length of the cyclobenzene molecule should be 1.753 Å, which is ~ 5% less than the length of the C—Si single bond in methylsilane (1.837 Å).[187] According to the results of the *ab initio* calculation (in terms of the STO-3G basis set), the conjugation energy in the silabenzene molecule is −22 kcal mol^{-1} (for the benzene molecule the calculated conjugation energy is −32 kcal mol^{-1} and agrees fully with experimental data).[188]

The somewhat more stable silatoluene had been obtained earlier by the dehydrochlorination (at −77 °C) of 1-chloro-1-methyl-1-silacyclohexa-2,4-diene[189] and the pyrolysis (at 450 °C) of 1-allyl-1-methyl-1-silacyclohexa-2,4-diene[190]. Silabenzene was obtained in 1980 by the pyrolysis of 1-allyl- and 1-acetoxy-1-silacyclohexa-2,4-dienes[191,192].

The published PES of these aromatic organosilicon compounds are of interest. In conformity with the relations noted above and found in a study of the PES of phosphabenzene and its analogues, the ionisation potentials of silabenzene should vary linearly with the ionisation potential of the 3*p* electrons of the silicon atom. The calculated ionisation potential of silabenzene and its value determined from the PES are similar:

I(calc.), eV (Ref.1)	8.2 ($\varphi_{\pi(\mathrm{sym})}$)	9.2 ($\varphi_{\pi(\mathrm{asym})}$)	11.5 (φ_{π_1})
I(exp.), eV (Ref.191)	8.0	9.3	11.3

This shows that five 2*p* electrons of the carbon atoms and one 3*p* electron of the silicon atom in the molecule of this compound are delocalised, in full agreement with the characteristics of the formation of aromatic systems. An analogous situation has been observed also in the case of silatoluene[193]. Two ionisation bands in its PES have been assigned: at 7.7 eV to the $\varphi\pi(\mathrm{sym})$ orbital and at 9.15 eV to the $\varphi\pi(\mathrm{asym})$ orbital.

In conformity with the considerably higher energies of the highest occupied molecular orbitals of silabenzene and silatoluene compared with their carbon analogues, the ultraviolet spectra of these compounds exhibit a distinct bathochromic shift of all the absorption bands. As in the ultraviolet spectrum of benzene, three absorption bands are observed in that of silabenzene (at 10 K in an argon matrix): at 212 nm (instead of 180 nm in the benzene spectrum), at 272 nm (instead of 203 nm), and at 315–320 nm (instead of 255–265 nm). The long-wavelength absorption in the ultraviolet spectrum of silatoluene is observed at 315 nm instead of 255–265 nm in the ultraviolet spectrum of toluene[192].

The first compounds with an sp^2-hybridised germanium atom, namely 4-ethyl, and 4-(t-butyl)germatoluenes, have also been synthesised by the pyrolysis of the corresponding cyclohexadienes and investigated by the PES method[194].

Silabenzene and silatoluene proved to be the first compounds with an sp^2-hybridised silicon atom which was sufficiently stable for their study by the PES method. The first communications concerning the synthesis of stable disilenes—compounds with a double bond between two silicon atoms—appeared in 1981–1982.[195–197] For example, tetramesityldisilene[196] $(Me_3C_6H_2)_2Si{=}Si(C_6H_2Me_3)_2$ was obtained by the photolysis of 2,2-dimesitylhexamethyltrisilane[196], while the photolysis of hexakis(2,6-dimethylphenyl)cyclotrisilane yielded the disilene $(Me_2C_6H_3)_2Si{=}Si(C_6H_3Me_2)_2$.[197] It has been shown by X-ray diffraction that the bond length between the silicon atoms in the first of these disilenes is shorter than a single silicon–silicon bond in polysilanes by 10% and its ultraviolet spectrum showed an absorption at a longer wavelength, namely at 272 nm (3.85), 340 nm (3.44), and 422 nm (3.8), compared with the ethylene analogue.

5. The Atoms of the Boron Subgroup Elements

Organic compounds of the boron subgroup elements are distinguished by a high reactivity: they readily oxidise in air, react with electron donors, and tend to polymerise. The corresponding boron compounds are somewhat less reactive. Their PES and their orbital structure have been investigated in greater detail.

The BC_3 fragment in the trimethylborane molecule is planar and the boron atom has orbitals assuming trigonal directions. The first band in the PES of this compound refers to the ionisation of the σ(B—C) orbital and is observed at 10.7 eV; the ionisation of the σ(C—H) orbital is observed at 12.8–14.5 eV.[198]

In the study of the PES of boranes in which the boron atom is linked to unsaturated fragments, attention was concentrated on the estimation of the role of the unoccupied 2*p* orbitals of the boron atom in the formation of the occupied molecular orbitals. Since the boron atom has unoccupied *p* orbitals with the same principal quantum number $n = 2$ as the carbon atom, its corresponding compounds constitute a convenient model for the estimation of the role of the unoccupied orbitals in bonding, particularly in view of the ambiguity of the conclusions concerning the role of the unoccupied *d* orbitals in compounds of the elements in the Third and higher Periods[13–16].

The first attempt to estimate the involvement of the unoccupied *p* orbitals of boron in the interaction with the π orbitals of carbon was undertaken in connection with the comparison of the PES of trivinyl- and triethyl-boranes[199]. The first ionisation potentials of these compounds proved to be virtually identical, namely 9.7 and 9.6 eV respectively, and the ionisation of the π electrons in trivinylborane begins at 10.7 eV, as in ethylene. According to the authors[199], no appreciable mixing of the unoccupied 2*p*(B) orbitals with the π orbitals of the vinyl groups is observed in trivinylborane either as a consequence of the displacement of the orbitals from the plane (with conservation of the sp^2-hybridisation of the boron atom) or owing to the pyramidal structure of trivinylborane.

The involvement of the unoccupied 2*p* orbitals of the boron atom in the formation of the molecular orbitals of phenylboranes has been estimated by Ramsey and O'Neil[200]. As in the case of, for example, phenylsilanes $PhSiX_3$,[179] where the *d* orbitals play a significant role in the formation of the molecular orbitals, a dependence of the contribution of the unoccupied 2*p*(B) orbitals to the molecular π orbitals of the phenylboranes $PhBX_3$ on the character of the substituents X is observed. Fig.2 compares the energies of the π orbitals of various phenylboranes of the type $PhBX_2$. For example, in the PES of $PhBR_2$ the first ionisation potential refers to the ionisation of the a_2 orbital, whose energy increases as a consequence of the electron-donating influence of the group BR_2. It has been found from the results of a

quantum-chemical calculation that the contribution of the $2p$(B) orbital to the $\pi(b_1)$ orbital is considerable and the energy of the molecular orbital is therefore reduced.

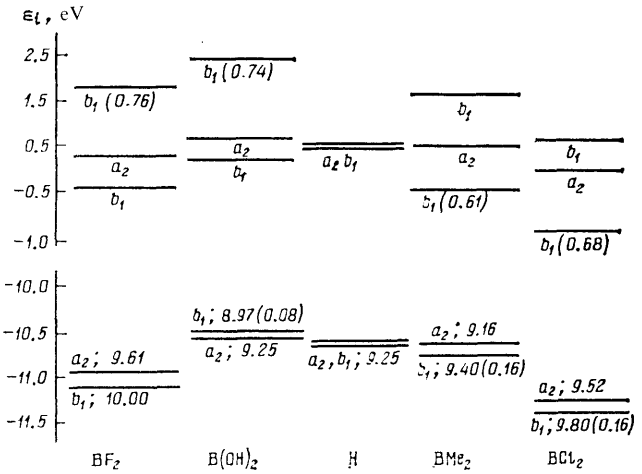


Figure 2. The influence of the substituents BX_2 on the energies of the π orbitals of the phenylboranes $C_6H_5BX_2$ according to PES data (the ionisation potentials are indicated in electron-volts) and CNDO/2 calculations [the energies of the molecular orbitals are indicated along the ordinate and the coefficients of the $2p$(B) orbitals in the corresponding molecular orbitals are indicated in brackets][200].

It was established in the same study[200] that the $2p$(B) orbital makes a considerable contribution to the occupied π orbitals also in dichlorophenylborane. As a consequence of the π-donor influence of the oxygen and fluorine atoms, the degree of involvement of the $2p$(B) orbital in the occupied $\pi(b_1)$ orbitals in the compounds with X=OR and F is reduced but becomes considerable in the unoccupied $\pi^*(b_1)$ orbitals.

6. The Atoms of the Zinc Subgroup Elements

Compounds in which the metal atom is bound to organic groups are known for virtually all the Group II metals. The reactivity of the organic compounds of the beryllium subgroup metals is, however, appreciably higher as a result of which their structure has been scarcely investigated by the PES method. On the other hand, although the zinc subgroup metal atoms have appreciably lower electronegativities than carbon, their organic, including aromatic, compounds are much less reactive; they have found wide applications in organometallic synthesis and are classical objects in theoretical chemistry[201,202]. The mixing of the orbitals in these compounds, in the first place in mercury compounds, has been studied in fair detail.

The C—E—C angles in dialkyl derivatives of Group IIB metals are ~ 180°[78] and the carbon–metal σ-bonds have low ionisation potentials[203–208]; the ionisation potentials of dimethylmercury, for example, are 9.3 and 11.6 eV[203,208]. Both properties specified above promote the mixing of the atomic orbitals of Group IIB metals with the carbon π orbitals in the corresponding organometallic compounds.

The role of the interaction of the σ and π orbitals in the benzyl and allyl compounds of mercury containing the



C=C—C—Hg fragment was first noted by Nesmeyanov as early as 1948[209]; a molecular-orbital interpretation of the effect of the σ—π conjugation was first achieved in a study of the absorption spectra of charge-transfer complexes[210]; quantitative estimates of the degree of mixing of the σ(C—Hg) and π orbitals in allyl and benzyl compounds of mercury were achieved only when PES was employed[211–218].

In particular, in a study of the PES of allylmercury chloride, Schmidt et al.[211] estimated the degree of mixing of the σ(C—Hg) and carbon π orbitals with the aid of the quantity δE determined from the formula

$$\delta E = (H_{\sigma\pi})^2/\Delta E ,$$

in which ΔE is the difference between the energies of the fragment orbitals and $H_{\sigma\pi}$ the resonance integral for the σ and π orbitals. The values of $H_{\sigma\pi}$ calculated from the PES data for allylmercury chloride and benzylmercury chloride proved to be virtually identical (0.98 and 0.99 eV respectively) and close to the corresponding values for the allyl and benzyl compounds of other metals[212].

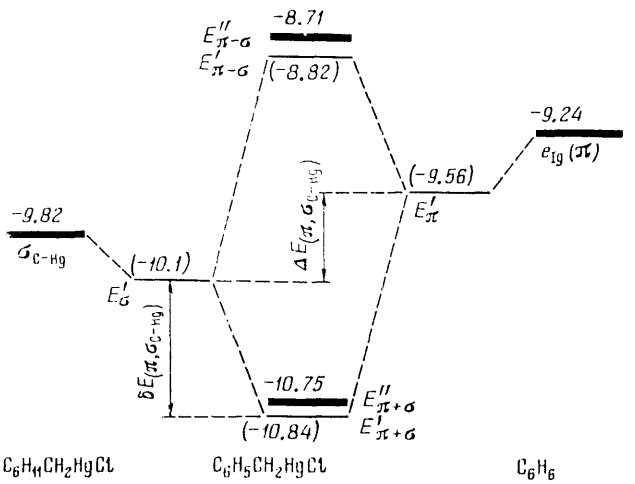


Figure 3. Schematic illustration of the formation of the molecular orbitals of benzylmercury chloride[213] (the energies are indicated in electron-volts).

An attempt has been made[213] to separate the contributions to the molecular orbital energy due to the σ(C—Hg)—π mixing, the inductive effect, and the mixing of the σ(C—Hg) and π orbitals with the σ(C—H) orbitals. Fig. 3 presents a qualitative diagram for the formation of the molecular orbitals of benzylmercury chloride. The value of E(C—Hg) shown in this diagram was found from the correlation between the ionisation potentials of the n(Cl) and σ(C—Hg) orbitals established on the basis of data referring solely to alkylmercury chlorides; the values of E'_{σ}(C—Hg) and E'_{π} were estimated taking into account the inductive effects of the Ph and CH_2HgCl groups respectively; the energies $E'_{\sigma-\pi}$ and $E'_{\sigma+\pi}$ were found from equations proposed[37] for a quantitative description of the σ—π mixing; the energies $E''_{\sigma-\pi}$ and

$E''_{\sigma+\pi}$ were estimated with the aid of the corresponding ionisation potentials found from the PES of benzylmercury chloride. The difference between the values of $E'_{\sigma-\pi}$ and E'_{π} is equal to the absolute change in the energy of the benzene $b_1(\pi)$ orbital arising owing to its mixing with the σ(C—Hg) orbital and the value 0.74 eV was adopted for it. The differences between the $E''_{\sigma-\pi}$ and $E'_{\sigma-\pi}$ energy levels and also between $E''_{\sigma+\pi}$ and $E'_{\sigma+\pi}$ are associated with the additional destabilisation of the molecular orbitals on mixing of the initial σ(C—Hg) and π orbitals with σ(C—H) orbitals.

It is of interest to compare the values of the integral $H_{\sigma(C-H)\pi}$, characterising the degree of mixing of the σ(C—Hg) and π orbitals, obtained in two ways. One value was found from the data in the diagram (Fig. 3):

$$H_{\sigma(C-Hg)\pi} = \sqrt{(-9.56+8.82)(-10.1+8.82)} = -1.0 \text{ eV}.$$

The other, amounting to −1.1 eV, was found from the scheme discussed in the Introduction, i.e. without including the additional effects noted in the diagram but with an appropriate selection of model compounds for the estimation of the energies of the fragment orbitals: the energy of the π orbital was estimated with the aid of the first ionisation potential of benzene, while the first ionisation potential of methylmercury chloride was used to estimate the energy of the σ(C—Hg) orbital[214]:

$$H_{\sigma(C-Hg)\pi} = \sqrt{(-9.24+8.71)(-10.8+8.71)} = -1.1 \text{ eV}.$$

Without overestimating the similarity of the above two estimates of the integral $H_{\sigma(C-H)\pi}$, we emphasise yet again that, with an apt selection of "model" compounds, it is as a rule possible not only to parametrise reliably the quantum-chemical calculations for the corresponding complex compounds on the basis of the PES of the "model" compounds[108] but also one can estimate fairly reliably the degree of mixing of particular atomic or fragment orbitals.

There are few data for the orbital interactions in compounds where the mercury atom is linked directly to carbon π-electron systems[213,218,219]. The ionisation potentials (eV) of phenylmercury chloride PhHgCl [9.40 ($b_1 + a_2$); 10.45 (σ_{C-Hg}); 10.84 (p_{Cl})] and phenylmercury bromide PhHgBr [9.33 ($b_1 + a_2$)] show that the occupied 5*d* and unoccupied 6*p* atomic orbitals of mercury are not effectively mixed with the benzene π orbitals. The same conclusion is valid also for diphenylmercury[219]. On the other hand, the mixing of the e_{1g}—π orbitals of propynyl groups and the e_{1g}($5d_{xz}$ and $5d_{yz}$) orbitals of mercury in mercurialkynes has been observed.

The PES method and the quantum-chemical calculations in the π-approximation parametrised on its basis make it possible to estimate quantitatively the degree of mixing of the orbitals of various elements with the carbon π orbitals in the corresponding organoelemental aromatic compounds. The estimates obtained show that the main factor determining the effectiveness of the mixing is the principal quantum number of the element, i.e. the number of the Period to which it belongs. The most effective π-type mixing with the π orbitals of carbon is that of the corresponding orbitals of the elements in the Second Period.

Nevertheless the atoms of elements having a principal quantum number greater than two are capable of $(p-p)\pi$ bonding both with carbon atoms and with one another contrary to the "classical double bond rule"[220-222]. The parameters $H_{E\pi(sym)}$ and $H_{(CE)\pi(sym)}$, characterising the mixing of the benzene $\phi_{\pi(sym)}$ orbital with the corresponding orbitals localised at the heteroatoms E, are fairly large, their values being listed below for certain Group IV—VII elements (see also Tables 1—3 and 6):

C	N	O	F
−1.03	−1.21	−1.37	−0.84
Si	P	S	Cl
−0.60	−0.34	−0.84	−0.63
Ge	As	Se	Br
−0.54	0.0	−0.72	−0.62

As shown in the present review, the parameters $H_{E\pi(sym)}$, determined from the analysis of the PES of "model" compounds (substituted benzene derivatives) determine unambiguously in their turn the parameters H_{EC} ($H_{EC} = \sqrt{3}H_{E\pi(sym)}$), which characterise the mixing of the orbitals of the element not with the benzene π orbital but with the $2p_{\pi}$ orbital of the carbon atom and are suitable for the estimation and parametrisation of the mixing of the orbitals also in calculations carried out in terms of an atomic basis set. The parameters H_{EC} have been used successfully in the analysis of the molecular orbital structure, particularly in the case of cyclic compounds where the atoms of the elements are present as part of the composition of rings and not as substituents[108-110,129].

The matrix elements $H_{\mu\mu}$ and $H_{\mu\nu}$, used in quantum-chemical calculations by the simple method, have a complex nature: they include also effects determined by the skeletal integrals and the effects of the interelectronic interactions. At the same time it is evident that the diagonal elements $H_{\mu\mu}$ and $H_{\nu\nu}$ depend mainly on the energy of the electron in the μth and νth fragment orbitals respectively, while the non-diagonal elements $H_{\mu\nu}$ depend mainly on the energy of the electron in the region of the mixing of the μth and νth fragment orbitals and thus characterise the degree of their interaction. The parameters $H_{\mu\nu}$, which have a perfectly definite quantum-chemical significance, can, in our view, provide a better understanding of the experimental results in many instances than the numerous constants estimating the conjugation effects. The molecular-orbital characteristics calculated on their basis have been used successfully in the interpretation of the spectra (in the first place photoelectron spectra) and reactivities of complex organoelemental aromatic compounds, including polycyclic compounds.

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