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$p\pi$-Conjugation in Aromatic Compounds of Group V and VI Elements

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The results of experimental and theoretical studies of intramolecular electronic interactions in aromatic compounds of group V and VI elements have been reviewed. The principal characteristics of their electronic structure, their geometry, and their electron-donor properties have been discussed. The possibilities provided by various methods (UV spectroscopy, NMR, PES, thermochemistry) for detecting and estimating the degree of combination of the unshared pair of electrons of the heteroatom with the π-electron system of the aromatic fragment have been analysed in detail. Quantitative estimates of the energy of $p\pi$-conjugation have been given.
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I. INTRODUCTION

The concept of the unshared electron pair is one of the most fundamental and widely used concepts in organic chemistry. This concept is used to explain various phenomena in the chemistry of aromatic and unsaturated compounds containing heteroatoms. The idea that the unshared electron pair (UEP) of the heteroatom interacts with the π-electron system of a neighbouring aromatic or unsaturated fragment makes it possible to explain many physical and chemical properties of the corresponding compounds. Various symbols and varied terminology are used in the scientific literature to characterise this type of intramolecular interatomic interaction. In the present review, the most widely encountered term, namely $p\pi$-conjugation, will be used.

In recent years the problem of $p\pi$-conjugation has been studied intensively by various physical methods, including photoelectron spectroscopy (PES), X-ray electron spectroscopy (XES), nuclear magnetic resonance (NMR), electron spectroscopy, etc. Together with quantum-chemical calculations, this information makes possible a deeper understanding of the nature of this interaction and enables the degree of interaction to be related to the structure and properties of the molecules. The degree of combination of the UEP of the heteroatom with the π-system determines to a large extent the electron-donor properties of compounds. The study of the electron-donor properties of aromatic compounds containing a heteroatom gives extensive information on the structure of their molecular orbitals (MO) and makes it possible in a number of cases to obtain quantitative estimates of the degree of $p\pi$-conjugation.

The present review analyses the most characteristic indications of $p\pi$-conjugation, and discusses the regular features of and differences in its manifestation in compounds of different elements for examples of simple molecules with typical compositions and structures, containing elements of groups V and VI. Particular attention has been paid to the questions of the coordination and changes in the structure of $p\pi$-conjugated molecules on complex formation.

Because of the vast amount of material, the literature in which the use of various methods to study $p\pi$-conjugated molecules is discussed has been examined selectively. Only those papers which contain information making it possible to estimate to some extent the degree of $p\pi$-conjugation have been included. The literature on the reactivity of $p\pi$-conjugated molecules (apart from their complex-forming power) is not discussed. Because of the large number of literature sources, reference is sometimes made not to an original paper but to a later review which gives references to the original work.

II. THE STRUCTURE OF $p\pi$-CONJUGATED MOLECULES AND THEIR COMPLEXES

1. The Electronic Structure and Conformations of $p\pi$-Conjugated Molecules

In the valence bond (VB) method, $p\pi$-conjugation is regarded as an intramolecular donor–acceptor interaction with charge transfer.[1,2] The donor fragment is the UEP of the heteroatom, and the acceptor fragment is the π-system of an aromatic group adjoining the heteroatom. The production of this interaction is determined to a large extent by the conditions of overlap of the orbital of the UEP of the heteroatom and the p_π-orbital of the carbon atom of the aromatic fragment joined to it.

In the molecular orbital method, the extent of the production of $p\pi$-conjugation is often related to the relative contributions of the atomic orbitals, including the orbital of the UEP of the heteroatom, to the highest occupied orbitals of the molecule. Mixing of the highest occupied π-orbital of the aromatic fragment with a UEP p_π-orbital of appropriate symmetry leads to the formation of two new orbitals, whose relative positions are represented schematically in the Figure (for the anisole molecule).[3] The Figure shows that the interaction of the UEP of the heteroatom with the aromatic fragment leads to an increase in the energy of the highest occupied MO of the molecule relative to the aromatic fragment.

The energy of the π-bond produced is determined by the value of the resonance integral (MO method) or the exchange integral (VB method), and depends on the degree of overlap of the corresponding orbitals of the fragments. The overlap of orbitals is usually estimated using the overlap integral, which depends on the angle between the axis of symmetry of the p-component of the UEP orbital and the axis of symmetry of the p_π-orbital of the neighbouring carbon atom of the aromatic fragment.[4] Thus both the MO method and the VB method make quite definite requirements of the state of the

interacting orbitals, both in relation to their energy and in relation to their relative orientation.

Both of these methods (VB and MO) are used to interpret the experimental data obtained by different physicochemical methods. In the study of properties related to the excitation of the molecules and one-electron transitions (electronic spectra, photoelectron spectra, etc.), the MO method is usually employed.

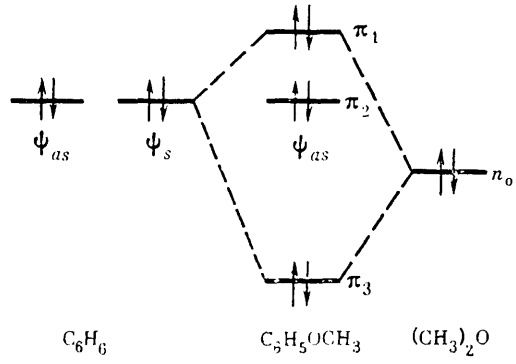


Diagram of the energy levels in the anisole molecule.[3]

The E atom in compounds of elements of group VI of the type ArER has two UEP. From the symmetry and energy of the atomic orbitals, it is assumed[3] that $p\pi$-interaction involves the UEP in the p_z-AO of the E atom. The extent of this interaction has been estimated[5] using the values of the resonance integrals β_{E-C}, which in compounds of the type $C_6H_5ECH_3$ decrease in the order O > S > Se > Te.

The heteroatom of tervalent compounds of group V elements has one UEP. The contribution of the p_z-orbital to the orbital of the UEP of compounds of group V elements can be estimated from the value θ of the C–E–C valence angle:[6]

$$p,\ \% = \frac{3\cos\theta}{\cos\theta - 1} \cdot 100$$

The average values of the valence angles θ in triaryl derivatives of group V elements, obtained by X-ray diffraction, are given below.

Compound	N	P	As	Sb	Bi
$(C_6H_5)_3E$	119.6 (Ref.7)	103.0 (Ref.8)	100.1 (Ref.9)	—	94 (Ref.10)
$(4\text{-}CH_3C_6H_4)_3E$	119.9 (Ref.11)	101.7 (Ref.12)	99.3 (Ref.13)	97.3 (Ref.14)	94.7 (Ref.15)

The practically planar (θ ≅ 120°) structure of the central fragment of triarylamines indicates that the UEP of the nitrogen atom in these compounds is in the *p*-state. In the compounds of other elements, the contribution of the *p*-orbital to the orbital of the UEP is appreciably smaller, and, judging from the values of the valence angles, decreases in the order N > P > As > Sb > Bi. It may be noted that the contributions of the *p*-component to the orbital of the UEP, obtained for phosphines from the values of the valence angles, are appreciably lower than those found from the results of non-empirical calculations[16,17] or determined from an analysis of the PES by CNDO/2 calculations.[18]

Thus the orbital of the UEP in compounds of group V elements contains an appreciable contribution from the *p*-orbital, so that it is capable of reacting to some extent with a neighbouring π-system. The values of the overlap integrals of the Slater orbitals, calculated (as in Ref.19) with

Table 1. Geometric parameters of various amines, phosphines, ethers, and sulphides.

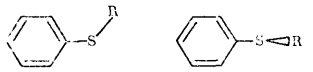
No.	Compound	*R*(E–C), Å	θ°	Other parameters	Method	Refs.
(I)	CH_3NH_2	1.474	HNH 105.9; CNH 112.0	—	MW	[32]
(II)	$C_6H_5NH_2$	1.402	HNH 113.1	τ=37.5°	MW	[33]
(III)	$4\text{-}ClC_6H_4NH_2$	1.39	HNH 137; CNH 111	—	XRD	[34]
(IV)	$4\text{-}NO_2C_6H_4NH_2$	N_{am}–C 1.362	—	—	MW	[35]
	»	N_{am}–C 1.371	120	φ=16°	XRD	[36]
(V)	$(CH_3)_2NH$	1.466	CNH 108.8; CNC 112.2	—	MW	[37]
(VI)	$4\text{-}FC_6H_4NHCH_3$	—	—	τ=18°	MW	[38,39]
(VII)	$(CH_3)_3N$	1.458	110.9	—	MW	[40]
(VIII)	$C_6H_5N(CH_3)_2$	N–C_{Ar} 1.43; N–C_{Alk} 1.46	116	τ=27°	MW	[41,42]
(IX)	$4\text{-}NO_2C_6H_4N(CH_3)_2$	N–C_{Ar} 1.36; N–C_{Alk} 1.50	120	φ=7.3°	XRD	[43]
(X)	$4\text{-}NO_2$, $2,6\text{-}Cl_2C_6H_2N(CH_3)_2$	N–C_{Ar} 1.41; N–C_{Alk} 1.46	120	φ=60.5°	XRD	[44]
(XI)	$(C_6H_5)_3N$	1.42	116	γ=47°	ED	[45]
		1.418	119.6	γ=44°	XRD	[7]
(XII)	$(4\text{-}CH_3C_6H_4)_3N$	1.419	119.9	γ=42°	XRD	[11]
(XIII)	CH_3PH_2	1.863	HPH 93.4; CPH 97.5	—	MW	[46]
(XIV)	$C_6H_5PH_2$	1.839	—	—	ED	[47]
(XV)	$(CH_3)_3P$	1.843	98.9	—	MW	[40,48]
(XVI)	$(C_6H_5)_3P$	1.828	103	γ=37°	XRD	[8]
(XVII)	$(4\text{-}CH_3C_6H_4)_3P$	1.832	101.7	γ=42°	XRD	[12]
(XVIII)	$(2\text{-}CH_3C_6H_4)_3P$	1.835	102.6	γ=45°	XRD	[49]
(XIX)	$[2,6\text{-}(CH_3)_2C_6H_3]_3P$	1.842	109.5	γ=42°	XRD	[50]
(XX)	$[2,4,6\text{-}(CH_3)_3C_6H_2]_3P$	1.837	109.7	γ=44°	XRD	[51]
(XXI)*	$[4\text{-}(CH_3)_2NC_6H_4]^{(1)}\text{-}P[(C_6H_5)_2]^{(2,3)}$	P–C 1.827; N–C_{Ar} 1.280; N–C_{Alk} 1.442	CPC 102.1; CNC 120	$\gamma^{(1)}$=37°; $\gamma^{(2)}$=55°; $\gamma^{(3)}$=38°	XRD	[52]
(XXII)	$(CH_3)_2O$	1.410	111.7	—	MW	[53]
(XXIII)	$C_6H_5OCH_3$	O–C_{Ar} 1.361; O–C_{Alk} 1.423	120	φ=0° (325 K); φ=40° (523 K)	ED	[54]
(XXIV)	$4\text{-}FC_6H_4OCH_3$	O–C_{Ar} 1.37; O–C_{Alk} 1.47	120	φ=6°	MW	[55]
(XXV)	$1,2,4,5\text{-}(CH_3O)_4C_6H_2$	O–C_{Ar} 1.380; O–C_{Alk} 1.424	117	φ=0°	XRD	[56]
(XXVI)	$1,4\text{-}(C_2H_5O)_2C_6H_4$	O–C_{Ar} 1.377; O–C_{Alk} 1.421	119.2	φ=0°	XRD	[57]
(XXVII)	$1,4\text{-}(CH_3O)_2C_6(CH_3)_4$	O–C_{Ar} 1.379; O–C_{Alk} 1.470	114.7	φ=87.9°	XRD	[58]
(XXVIII)	$[2,4\text{-}(NO_2)_2C_6H_3]^{(1)}\text{-}O[C_6H_2(t\text{-}C_4H_9)_3]^{(2)}$	O–$C^{(1)}$ 1.35; O–$C^{(2)}$ 1.43	116.8	$\varphi^{(1)}$=3.2°; $\varphi^{(2)}$=87.5°	XRD	[59]
(XXIX)	$(CH_3)_2S$	1.807	99.1	—	ED	[60]
(XXX)	$C_6H_5SCH_3$	S–C_{Ar} 1.749; S–C_{Alk} 1.803	105.6	φ=45.3°	ED	[61]
(XXXI)	$(C_6H_5)_2S$	1.771	103.7	—	ED	[62]
(XXXII)	$(4\text{-}CH_3C_6H_4)^{(1)}S(4\text{-}CH_3C_6H_4)^{(2)}$	1.75	109	$\varphi^{(1)}$=32.5°; $\varphi^{(2)}$=35.0°	XRD	[63]
(XXXIII)	$[3,4\text{-}(CH_3O)_2C_6H_3]^{(1)}\text{-}S[3,4\text{-}(CH_3O)_2C_6H_3]^{(2)}$	$S\text{–}C^{(1)}_{Ar}$ 1.779; S–$C^{(2)}$ 1.764; O–C_{Ar} 1.365; O–C_{Alk} 1.422	103.1	$\varphi^{(1)}$=3.6°; $\varphi^{(2)}$=90.9°	XRD	[64]
(XXXIV)	$(4\text{-}NO_2C_6H_4)^{(1)}S(C_6H_5)^{(2)}$	1.778(1); 1.779(2)	104	$\varphi^{(1)}$=2.3°; $\varphi^{(2)}$=84.3°	XRD	[64,65]
(XXXV)	$[4\text{-}(CH_3)_2NC_6H_4]^{(1)}\text{-}S(C_6H_5)^{(2)}$	S–$C^{(1)}$ 1.786; S–$C^{(2)}$ 1.769; N–C_{Ar} 1.380; N–C_{Alk} 1.449	CSC 104.1; CNC 118.7	$\varphi^{(1)}$=84.9°; $\varphi^{(2)}$=4.5°	XRD	[66]
(XXXVI)	$[4\text{-}(CH_3)_2NC_6H_4]^{(1)}\text{-}S(C_6H_4NO_2\text{-}4)^{(2)}$	S–$C^{(1)}$ 1.795; S–$C^{(2)}$ 1.780; N–C_{Ar} 1.355; N–C_{Alk} 1.432	CSC 105; CNC 118.7	$\varphi^{(1)}$=68.9°; $\varphi^{(2)}$=1.8°	XRD	[64,65]

Symbols: *R*(E–C) is the length of the E–C bond; θ the valence angle; τ the angle between the axis of the N–C_{Ar} bond and the bisector of the angle RNR (R = H, CH_3); φ the angle between the plane of the ring and the plane of the C–E–C angle; and γ the angle between the plane of the ring and the plane passing through the E–C_{Ar} bond and the axis of the UEP. Methods: MW = microwave spectroscopy, ED = electron diffraction, XRD = X-ray diffraction. The geometric parameters for identical atoms and groups, obtained by X-ray diffraction, have been averaged.

*Here and subsequently the superscript in brackets gives the number of the aromatic ring.

allowance for the values of the C–E–C angle in compounds of the type $(C_6H_5)_3E$, decrease in the order: N–C > P–C > As–C > Sb–C > Bi–C (0.185, 0.119, 0.093, 0.063, 0.040 respectively). The angles of rotation of the aryl fragments about the E–C bond were not taken into account, since they have similar values for all triphenyl and tri-*p*-tolyl derivatives of group V elements (γ = 37–47°, Table 1).[7–15]

The conformation of molecules of the type C_6H_5ER is determined to a large extent by the competition between two factors: $p\pi$-conjugation (which is a maximum for the planar conformation (A), $\phi = 0°$) and steric hindrance (which is a minimum for the orthogonal conformation (B), $\phi = 90°$).



(A) (B)

Depending on the contributions of these effects determining the barrier to the rotation of the ER group relative to the ring, an effective conformation with an angle of $0° \leq \phi \leq 90°$, and an equilibrium between planar and orthogonal conformers, may be produced. From data on the dipole moments (DM) and Kerr constants of anisole[20,21] and thioanisole[22] it was concluded that these compounds show conformational uniformity; the angles θ are 18°[20] and 23°[22] respectively.

At the same time, data obtained from an analysis of the temperature dependence of the Raman spectra of anisole indicate[23] that the system contains the conformers (A) and (B). The same conclusion was reached in a study of the PES of anisole;[24] the difference in the energies of the conformers (B) and (A) was estimated as 1.3 kcal mole^{-1}. From the observed splitting of the first band in the PES of a series of compounds of the type C_6H_5SR,[25] it was concluded that they show conformational non-uniformity in the gas phase. Estimation of the concentration of the conformers from the ratio of the intensities of the components of the complex PES band showed that the proportion of the planar conformer decreases with increase in the volume of the alkyl substituent R, and has the values 0.90, 0.40, 0.15, and 0.05 for R = CH_3, C_2H_5, iso-C_3H_7, and t-C_4H_9 respectively. Approximately the same ratio of conformers for the compounds C_6H_5SR was obtained from UV and NMR spectroscopy.[26,27] At the same time, other authors[28] consider that the analysis of the PES of these compounds does not indicate unambiguously whether increase in the volume of the alkyl group leads to a gradual increase in the angle ϕ or displaces the conformational equilibrium (A) $\rightleftarrows$ (B).

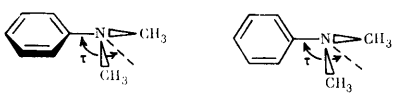
New classes of conformationally non-uniform alkylaromatic and unsaturated compounds of group V and VI elements have been described in recent papers. These include alkylaromatic compounds of selenium and tellurium,[3,29,30] alkyl phenyl ethers and sulphides containing different substituents,[3,30,31] and compounds of the type $(C_6H_5)_nPR_{3-n}$.[26,31] The difference in the energies ΔE_{A-B} of the conformers (A) and (B) is generally small. Thus for the compounds C_6H_5SR, the values for R = CH_3, C_2H_5, iso-C_4H_9, and t-C_4H_9 are −3.1, −1.4, −1.0, and 4.6 kJ mole^{-1}.[31] The comparatively small difference in the energies of the planar and orthogonal conformers of these compounds is apparently one of the reasons why they cannot be distinguished by certain methods. The methods examined below for estimating the energy of the $p\pi$-conjugation of aromatic compounds relate to the averaged characteristics of the geometry, and are interpreted in terms of the average value of the angle ϕ.

2. The Geometry of the Molecules of Aromatic Compounds of Group V and VI Elements

Intramolecular $p\pi$-interactions are reflected in the structural parameters of molecules. This question can be examined for the compounds of nitrogen and phosphorus (group V) and oxygen and sulphur (group VI).

Table 1 gives the bond lengths, valence angles, and various other structural parameters of the key fragments of molecules, obtained by microwave spectroscopy, gas-phase electron diffraction, and the X-ray diffraction study of crystals. The data for various aliphatic compounds are given for comparison. These are mainly the most reliable results obtained in recent years. Primary, secondary, and tertiary aliphatic amines ((I), (V), and (VII)) have a pyramidal configuration with an average value of the valence angle of the heteroatom (θ) of 110–111°. The pyramidal character of aromatic amines ((II)–(IV), (VI), (VIII)–(XII)) is much less marked, and the average value of the valence angle of the heteroatom is greater and for a number of compounds reaches 120°, that is the amino-group has the planar conformation (sp^2 hybridisation of the nitrogen atom), most favourable for $p\pi$-conjugation with the appropriate orientation of the aryl fragment.

The values of the angle ϕ in Table 1 show that in compounds (IV) and (IX) the ring and the amino-group are almost coplanar. The pyramidal (in the gas phase) molecules of aniline, N-methylaniline, N,N-dimethylaniline, and anilines containing substituents in the ring have the conformation (C), favourable for $p\pi$-conjugation.[33,38,39,41,42,67,68] For the molecule $C_6H_5CH(CH_3)_2$, the conformation (D) predominates.[69]



(C); $\gamma = 90°$ (D); $\gamma = 0°$

The influence of $p\pi$-conjugation is reflected not only in the valence angles and the conformation of the molecules but also in the E–C bond lengths. Thus the $N-C_{Ar}$ bond length in $p\pi$-conjugated molecules is appreciably shorter than $N-C_{Alk}$ (see Table 1). The bond length depends not only on the degree of double bond character but also on a number of other factors, such as the nature of the hybridisation of the orbitals and the electronegativities of the atoms forming the bond.[70] The increase in the $N-C_{Ar}$ bond length when there is steric inhibition of $p\pi$-conjugation or when aromatic amines are protonated (see below) shows, however, that the difference in the $N-C_{Ar}$ and $N-C_{Alk}$ bond lengths is determined chiefly by $p\pi$-conjugation.

In this connection, it is of interest to examine the structure of 2,6-dichloro-4-nitro-N,N-dimethylaniline (X).[44] In this molecule, for steric reasons, the $p\pi$-conjugation of the dimethylamino-group is prevented to a considerable extent; the angle between the plane of the amino-group and the ring is 60.5°. The $N_{am}-C_{Ar}$ bond length is 1.41 Å, which is much greater than in compound (IX) (1.36 Å) or in 3,5-dichloro-4-nitroaniline (1.37 Å).[44]

Gas-phase electron diffraction[45] has shown that the molecule of triphenylamine (XI) is slightly pyramidal (θ = 116°). X-Ray diffraction[7,11] has shown that the amine fragment of the crystalline amines (XI) and (XII) is planar ($\theta \cong 120°$). For steric reasons, however, triarylamines cannot have the conformation most favourable for $p\pi$-conjugation, with the ring and the amino-group coplanar. For triphenylamine, the values obtained for the angle γ are 47° from electron diffraction,[45] 44° from X-ray diffraction,[7] and 62° from data on the Kerr effect.[71]

In the molecules of crystalline *ortho*- and *para*-phenylenediamine, the amino-group has a pyramidal structure.[72,73] The non-planar structure of *ortho*-phenylenediamine (θ = 112.7°) was attributed[72] to the mutual repulsion of the two closely situated UEP and the location of these UEP on different sides of the plane of the ring. The presence of intermolecular H-bonds of the type N–H...N in *ortho*- and *para*-phenylenediamine crystals may influence the geometry of the amino-group.

The degree of pyramidal character of the aromatic phosphines (XVI)–(XXI) is lower than that of the aliphatic phosphines (XIII) and (XV). The valence angle of the phosphorus atom is ~102–103° for the sterically non-overcrowded triarylphosphines (XVI)–(XVIII) and (XXI), which corresponds to approximately *sp* hybridisation of the UEP of the phosphorus atom and indicates that the UEP of the phosphorus atom can be involved in $p\pi$-conjugation.[19] The angles of rotation of the rings (γ) for the triarylphosphines (XVI)–(XXI) differ little from the corresponding angles of rotation for the triarylamines (XI) and (XII) and is ~40°. From data on the Kerr effect, the angle γ for triphenylphosphine in solution is 59°.[71]

The steric effects of phosphorus-containing ligands in transition metal complexes have been analysed.[74] The steric effects of phosphines increase in the order: $(CH_3)_3P$ < $(C_2H_5)_3P$, $(C_3H_7)_3P$ < $(C_6H_5)_3P$, (iso-$C_4H_9)_3P$ < (iso-$C_3H_7)_3P$ < $(C_6H_{11})_3P$ < (t-$C_4H_9)_3P$ < [2,4,6-$(CH_3)_3C_6H_2]_3P$. The greatest steric effect is observed for trimesitylphosphine. The introduction of CH_3 groups in positions 2 and 6 of each ring of triphenylphosphine leads to a sharp increase (to 109.5°) in the valence angle of the phosphorus atom both in the crystalline phase (XIX) and (XX) (see Table 1) and in solution.[75] The average value of the angle γ differs little from that for triphenylphosphine. An increase in the valence angle of the heteroatom is also observed when two CH_3 groups are introduced in the *ortho*-positions of each ring of triphenylarsenic,[76] triphenylantimony,[77] and triphenylbismuth.[78]

The conformation of phenylphosphines is not yet clear. According to electron diffraction data, the molecules of $C_6H_5PH_2$ and $C_6H_5PCl_2$ have the conformation (D) with angle γ = 0°,[47,69,79] and the $C_6H_5PF_2$ molecule has a conformation with an angle γ = 31°.[80] Data on the Kerr effect do not make it possible to reach definite conclusions about the conformation of dialkylarylphosphines in solution.[31,81–83] Recent data[26,31] indicate that an equilibrium between the conjugated (C) and non-conjugated (D) conformers is established in solution. The data in Table 1 show that the P–C_{Ar} bond is shorter than P–C_{Alk}, but the difference is much smaller than in the case of amines; this question will be examined below.

The C–E–C valence angle in the sterically non-overcrowded aromatic ethers (XXIII)–(XXVI) and sulphides (XXX)–(XXXVI) is much larger than in the corresponding aliphatic compounds (XXII) and (XXIX).[69] The crystalline aromatic ethers (XXIII)–(XXVI) have the planar conformation (A) (ϕ = 0°) favourable for $p\pi$-conjugation. In the gas phase at a temperature of 325 K, anisole has an almost planar conformation; with increase in temperature to 523 K, the geometry of the anisole molecule changes considerably, and the angle ϕ increases to 40°.[84] The lower ability of sulphur and selenium atoms, compared with oxygen, to take part in $p\pi$-conjugation leads to much larger values of the angle ϕ in thioanisole (XXX) (45.3°) and selenoanisole (40°).[84] Data on the Kerr effect indicate that anisole,[20] thioanisole,[22] and selenoanisole[85] have non-planar structures, and that the angle ϕ increases in the order indicated. When electron-acceptor substituents (for example NO_2) are introduced into the *para*-position, the $p\pi$-conjugation of the O, S, and Se atoms with the ring increases, and the angle ϕ decreases.[20,22,85]

The coplanarity of the ring and the methoxy-group may be destroyed by steric factors. *para*-Dimethoxybenzene[86] and *para*-diethoxybenzene (XXVI) have planar structures. The introduction of four bulky substituents, CH_3 (XXVII), and also Cl and Br,[87] into the 2,3,5,6-positions of the ring displaces the methoxy-groups from the plane of the ring (ϕ = 84–88°); the valence angle of the oxygen atom decreases to 114.5°, and the $p\pi$-conjugation is destroyed.[88] The conformation of compounds containing two methoxy-groups in the *ortho*-position to one another apparently depends on the state of aggregation. In the crystalline state, the molecules are planar (XXV), but in the gas phase, one of the methoxy-groups is coplanar with the ring, but the second is not.[86] The conformation of these molecules in solution is not clear.[89,90]

A coplanar arrangement of the two phenyl rings and the plane of the CEC angle in diphenyl ether and diphenyl sulphide is impossible, for steric reasons. If one of the rings is coplanar with the plane of the CEC angle (ϕ = 0°), the second ring forms an angle ϕ = 70–90° with this plane, (XXVIII) and (XXXIII)–(XXXVI). The introduction of an electron-acceptor substituent into one of the rings of diphenyl sulphide (XXXIV) facilitates $p\pi$-conjugation of the substituted ring, as indicated by the value of the angle $\phi^{(1)}$ = 2.3°, whereas the angle $\phi^{(2)}$ for the non-substituted ring is 84.3°. On the other hand, the introduction of an electron-donor substituent into one of the rings (XXXV) leads to coplanarity of the CSC group and the non-substituted ring. In the diaryl sulphide (XXXVI), the CSC plane is coplanar with the ring containing the nitro-group ($\phi^{(2)}$ = 1.8°) and makes an angle of 68.9° with the ring containing the dimethylamino-group. If the substituents are identical, the angles $\phi^{(1)}$ and $\phi^{(2)}$ may be similar (XXXII) or different (XXXIII); this apparently depends on the packing conditions in the crystals. In this connection it should be noted that electron diffraction[62] did not make it possible to conclude that diphenyl sulphide has a definite conformation in the gas phase. This agrees with the idea that molecules of the type Ar_2E are non-rigid. The two equivalent aryl rings can rotate relative to one another about the E–C_{Ar} bonds. A non-rigid structure has been proposed for diphenyl ether.[91,92]

3. Changes in the Structure of Molecules on Complex Formation

The extent of the rearrangement of the molecules of electron donors on complex formation depends on the type of complex formed and the strength of the electron acceptor. Complexes with compounds of group III elements will be examined, since in the interaction with these acceptors, the geometry of aromatic compounds containing a heteroatom undergoes a rearrangement leading to breakdown of the $p\pi$-conjugation.[93] Breakdown of the $p\pi$-conjugation in aromatic amines and phosphines has also been observed when a H-bond is formed with strong carboxylic acids and on protonation.[19,94,95]

Gillespie's theory[96] predicts that when a complex is formed, the valence angle of the heteroatom of an acceptor should decrease, and the length of the bonds should increase. On the other hand, the valence angle of the heteroatom of a donor should increase, and the length of the bonds should decrease. The changes in the geometry of trimethylphosphine on complex formation with BH_3 (Table 2) agree with this prediction. The differences in the valence angles and bond lengths of the original trimethylphosphine and triphenylphosphine practically disappear when complexes are formed with BH_3 (Table 2). The geometry of the R_3P frag-

ments of trimethylphosphine and triphenylphosphine in the complexes is close to that of the R_3P fragments in phosphine oxides. All this indicates that the differences in the geometry of trimethylphosphine and triphenylphosphine are related to the $p\pi$-conjugation in the molecule of the latter. This applies particularly to the P–C bond length. In tetravalent phosphorus compounds there are no differences in the P–C_{Ar} and P–C_{Alk} bond lengths.[102]

Table 2. Geometric parameters of various phosphines, phosphine oxides, and complexes with BH_3.*

Compound	θ, °	R(P-C), Å	R(P-B) or R(P-O), Å	Method	Refs.
$(CH_3)_3P$	98.9	1.843	—	MW	[48]
$(C_6H_5)_3P$	103.0	1.828	—	XRD	[8]
$(CH_3)_3P\cdot BH_3$	105.0	1.819	1.901	MW	[97]
$(C_6H_5)_3P\cdot BH_3$	106.3	1.820	1.917	XRD	[98]
$(CH_3)_3PO$	104.1; 106.0	1.809; 1.81	1.476; 1.48	ED	[99, 100]
$(C_6H_5)_3PO$	106.2	1.82	1.49	XRD	[101]

*For symbols see Table 1.

Aromatic phosphines, particularly triphenylphosphine, are widely used as ligands in transition metal complexes. Many of these complexes have been studied by X-ray diffraction. The value of the C–P–C angle of the phosphorus atoms in both aliphatic and aromatic phosphines in transition metal complexes varies over a wide range (100–108° in triphenylphosphine); here, an important role is played by the strength of the coordinate bond and steric effects.[74,103]

Aliphatic amines undergo slight rearrangement on complex formation, and, in contrast to the case of aliphatic phosphines, the nature of the rearrangement does not agree with Gillespie's theory. Thus the C–N–C angle in the molecule of trimethylamine (110.9°) decreases in the complexes with compounds of group III elements to 108–111°, and the N–C bond length increases from 1.458 Å to 1.47–1.49 Å. The reasons for this anomaly are discussed, for example, in Refs. 104–106.

Table 3. N–C bond lengths in protonated (R_1) and non-protonated (R_2) aromatic amines.

Compound	R_1, Å	R_2, Å
$4\text{-}NO_2C_6H_4NH_2\cdot HCl$	1.472 [110]	1.371 [36]
$1,2\text{-}(NH_2)_2C_6H_4\cdot HCl$	1.460 [111]	1.391* [111]
$1,2\text{-}(NH_2)_2C_6H_4\cdot 2HBr$	1.445 [112]	1.407 [72]
$1,4\text{-}(NH_2)_2C_6H_4\cdot 2HCl$	1.463 [113]	1.408 [73]
$(C_6H_5)_2N(CH_2)_2\overset{+}{N}\overset{C_6H_5}{\underset{C_6H_5}{<}}CH_3\ I^-$	$N-C_{Ar}$ 1.497; $N-C_{Alk}$ 1.502 [114]	$N-C_{Ar}$ 1.414*; $N-C_{Alk}$ 1.451 [114]

*N–C bond length in the neutral amino-group of the complex.

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

There are no published data on the structure of complexes of aromatic amines with compounds of group III elements, but X-ray diffraction studies of transition metal complexes indicate that there is considerable rearrangement of aromatic amines on complex formation. As in the case of phosphines, the differences in the geometry of aliphatic and aromatic amines disappear on complex formation. The C–N–C valence angles decrease from 120° in the free aromatic amine to tetrahedral in a complex, and the N–C_{Ar} bond length increases sharply, becoming equal to the N–C_{Alk} bond length. Similar structural changes were observed for the molecule of N,N-dimethylaniline on complex formation with copper compounds,[107] for aniline and 4-toluidine in their complexes with nickel compounds,[108] and for 4-toluidine in its complex with CdI_2.[109]

Table 3 gives the N–C_{Ar} bond lengths in protonated aromatic amines and the N–C_{Ar} bond lengths for the corresponding neutral molecules. Protonation or methylation of the amino-group leads to a considerable increase in the N–C_{Ar} bond length to 1.45–1.50 Å, that is to a value characteristic of N–C_{Alk} bonds. The observed effect is evidently related to the breakdown of $p\pi$-conjugation on protonation of the aromatic amines.

III. THE ELECTRON-DONOR PROPERTIES OF AROMATIC COMPOUNDS OF GROUP V AND VI ELEMENTS

1. π-Donor Properties

Donors having a heteroatom with an UEP and a system of π-bonds can be divided into two groups. A characteristic feature of the molecules of one group is that the UEP of the corresponding heteroatom is not joined directly to the π-system of the molecule (pyridine, aryl ketones, etc.). In the molecules of the second group, the UEP of the heteroatom is included in the conjugated system (furan, thiophene, anisole, etc.).

The donors of the two groups behave differently towards different acceptors. The first group of donors, in their reactions with σ-acceptors (I_2, ICl, etc.) and ν-acceptors (BF_3, $AlCl_3$, $SnCl_4$, etc.) show the properties of n-donors, that is the intermolecular bond involves the free UEP of the heteroatom.[93] In their reaction with π-acceptors, the donors of the first group show π-donor properties.[93] In compounds of the second group, the UEP of the heteroatom is not free, but is involved in $p\pi$-conjugation. These compounds are weaker n-donors than the corresponding aliphatic compounds (see below). This is illustrated by the compounds furan and thiophene, which do not show n-donor properties and which form π-complexes not only with π-acceptors but also with σ- and ν-acceptors.[115,116] The symmetry and energy of the MO of analogues of furan have been discussed.[117]

The electronic spectra of complexes of aromatic and heteroaromatic π-donors with π- and σ-acceptors may contain two (and sometimes more) charge-transfer bands, as a result of the participation in complex formation of not only the HOMO but also lower-lying orbitals of the π-donor. As shown in the Figure, transitions from the π_1 and π_2 orbitals of the donor molecule are most probable.[115,118–122] The relative arrangement of the energy levels of the π-donor (see Figure) is determined by a number of factors, and primarily by the energies of the UEP of the heteroatom and the π-system.[3] The structure of the MO in aromatic compounds of group VI elements, of the type $C_6H_5ECH_3$, $XC_6H_4ECH_3$, XC_6H_4ER, etc. (from the electronic spectra of charge-transfer complexes of tetracyanoethylene and iodine and quantum-chemical calculations) has been discussed in a number of papers (see Refs. 3 and 123–126 and references therein).

The complexes of aromatic compounds of group V elements with π-acceptors (except nitrogen compounds) have been less extensively studied, and the available data are somewhat contradictory. The question of whether the complexes of aromatic amines with nitrobenzenes are π-complexes, n-com-

plexes, or complexes with an H-bond has not yet been resolved.[127] It is not clear whether the $p\pi$-conjugation is destroyed when I_2 forms complexes with aromatic amines, that is whether the molecular compounds formed are n,σ- or π,σ-complexes.[93,128]

Complex formation by aromatic amines with various π-acceptors is accompanied by chemical reactions. The latter often depend on the conditions of the experiment. Low temperatures and inert solvents stabilise π,π-complexes.[129–132] Triarylphosphines react with tetracyanoethylene in dichloroethane in the same way as amines, that is π,π complexes are formed first, after which reactions take place.[133] A similar study[134] of the complexes of $(C_6H_5)_3N$, $(C_6H_5)_3P$, and $(C_6H_5)_3$. .As with tetracyanoethylene in chloroform, however, led to the conclusion that the complexes formed are stable. As in the case of the complexes of tetracyanoethylene with aromatic ethers and sulphides, the spectra of these complexes contain two charge-transfer bands, which were assigned to transitions from the two highest MO of the donor to the LUMO of the acceptor.

Since the chief characteristics of the charge-transfer bands in the spectra of charge-transfer complexes are determined by the highest occupied orbitals of the donor molecule, it is natural to look for correlations between the energies of these bands ($h\nu$) and the ionisation potentials (IP) of the donors. For many classes of compound of group VI[3,115,119,128,131,135,136] and V [131,133,134] elements, a linear correlation has been observed between $h\nu$ and IP. This relationship has been widely used to determine IP from $h\nu$ data for charge-transfer complexes. The question of the range within which a linear correlation is observed between $h\nu$ and IP has been examined.[1,93,137]

The participation of several MO of a donor in electron transitions has been used[138–140] to explain the differences in the structures of the complexes formed, for example the "longitudinal" and "transverse" orientation of the tetracyanoethylene molecule relative to the phenyl ring in complexes with substituted benzenes. The relative orientation of the molecules of the donor and acceptor in π,π- and π,σ-complexes, as in complexes of other types, is determined to a large extent by the principle of maximum overlap of the interacting orbitals.[1,93] Of the two highest MO of aromatic compounds containing a heteroatom, only one contains a contribution from the UEP of the heteroatom (see Figure) and hence is localised in the region of the $E-C_{Ar}$ bond. The second orbital of π-symmetry is localised in the hydrocarbon fragment.[117,121] Different orientations of the acceptor molecule in the complex are possible, depending on which of these two orbitals overlaps the orbital of the acceptor. Evidence in support of this approach is provided, for example, by the results of an X-ray diffraction study of the charge-transfer complex of fluoranil with N,N-dimethylaniline.[141] In this case, two orientations of the fluoranil molecule were detected: in one of them, the ring of the acceptor is positioned directly above the phenyl ring of the donor, and in the other it is directly above the dimethylamino-group; judging from the distances between the donor and acceptor, the interaction in the latter case is stronger than in the former.

The energy of formation of π,π-complexes is generally low (~1–3 kcal mole^{-1}),[119,129,132] and the extent of charge transfar in the ground state of the complex does not exceed ~0.05;[119,120] complex formation in these systems is not accompanied by a significant rearrangement of the molecules of the donor and acceptor.[142–144] This makes it possible to use the electronic spectra of charge-transfer complexes to study intramolecular electronic interactions in organic and organometallic compounds.[145]

2. *n*-Donor Properties. The Determination of the Energy of $p\pi$-Conjugation by the Method of Complex Formation

On π-complex formation, aromatic compounds containing a heteroatom do not undergo appreciable rearrangement; the system of MO formed as a result of $p\pi$-conjugation is preserved. A fundamentally different picture is observed in the reaction of these compounds with strong electron acceptors (the halides of group III elements, strong carboxylic acids, etc.). The donor–acceptor bond is formed by the UEP of the heteroatom of the donor and an unoccupied orbital of the acceptor. The $p\pi$-conjugation is destroyed, the MO system of the original aromatic compound breaks down, and and an MO system characteristic of the aromatic fragment of the molecule is produced. A good illustration of this is provided by the changes in the electronic spectra of aromatic amines, ethers, phosphines, and sulphides on complex formation with strong acceptors (see below)

Some physicochemical properties and geometric characteristics (see above) of complexes of strong acceptors with aromatic and corresponding aliphatic *n*-donors are similar. These are the properties which are determined by the strength of the donor–acceptor bond ($-\Delta H_{DA}$) and the magnitude of the charge transferred from the donor to the acceptor. One such parameter is the dipole moment of the donor–acceptor bond (μ_{DA}) and (other conditions being equal) the dipole moment of the complex as a whole (μ_c), and also the extent of charge transfer from the donor to the acceptor μ_{DA}/er_{DA} (r_{DA} is the length of the donor–acceptor bond), determined from the value of μ_{DA}. Some examples are given in Table 4. The dipole moments of the complexes of the halides of boron, aluminium, and gallium with aliphatic and aromatic *n*-donors (amines, ethers, phosphines, sulphides) differ little from one another.[19,93,146]

Table 4. Dipole moments (μ_c, D) and enthalpies of formation of the complexes $D.AlBr_3$($-\Delta H$, kcal mole^{-1}).[19,146] *

D	μ_c	$-\Delta H$	$\Delta\Delta H$**	D	μ_c	$-\Delta H$	$\Delta\Delta H$**
Alk_2O	7.2 (av)	23.3 (av)	—	Alk_3N	8.6 (av)	32.3 (av)	—
$C_6H_5OCH_3$	7.00	15.9	7.4	$C_6H_5N(CH_3)_2$	8.68	24.2	8.1
$(C_6H_5)_2O$	7.29	12.0	11.3	$(C_6H_5)_2NCH_3$	8.01	17.4	14.9
Alk_2S	7.6 (av)	17.5 (av)	—	Alk_3P	10.2 (av)	32.2 (av)	—
$C_6H_5SCH_3$	7.00	13.1	4.4	$C_6H_5P(C_3H_7)_2$	—	27.7	4.5
$(C_6H_5)_2S$	7.55	10.2	7.3	$(C_6H_5)_3P$	10.0	21.3	10.9

*Some of the $-\Delta H$ values have been refined by the present authors.
**See the text for the significance of $\Delta\Delta H$.

A characteristic feature of donor–acceptor complexes is the relationship between the magnitude of the transferred charge and the energy of the donor–acceptor bond.[93] This is revealed by the linear relationship between the enthalpy of formation of the complex ($-\Delta H_c$) and the extent of charge transfer from the donor to the acceptor. For the complexes of aluminium and gallium compounds with aliphatic *n*-donors, the relationship has the form:[147]

$$-\Delta H_c \text{ kcal mole}^{-1} = 69.2\,\mu_{DA}/er_{DA} - 1.6 \qquad (1)$$

For the complexes with carboxylic acids, a similar relationship is observed:[148]

$$-\Delta H_c \text{ kcal mole}^{-1} = 38.0\,\mu_{DA}/er_{DA} + 3.9 \qquad (2)$$

According to Eqns.(1) and (2), complexes with identical degrees of charge transfer should have identical enthalpies of formation. The values of $-\Delta H_c$ for complexes of aromatic and corresponding aliphatic *n*-donors with the same acceptor should therefore be similar. It can be seen from Table 4, however, that the values of $-\Delta H$ for complexes with aromatic compounds are much lower than those for aliphatic compounds. This has been established for a wide range of complexes of strong acceptors with amines,[93,94,146] ethers, sulphides,[93,146,147,150,151] and phosphines.[19,93,147,149] The observed difference ($\Delta\Delta H$) in the values of $-\Delta H$ are due to the expenditure of energy in the rearrangement of the aromatic *n*-donor on complex formation, that is in the breakdown of $p\pi$-conjugation.

Thus the study of complex formation opens up a route for determining the values of the energy of $p\pi$-conjugation (E_c). In the simplest and crudest version, the energy of $p\pi$-conjugation can be estimated as the difference ($\Delta\Delta H$) in the values of $-\Delta H$ for the complexes of a given acceptor with aliphatic and corresponding aromatic donors.[19,88,93,94,146,149,150] The values of $\Delta\Delta H$ for each aromatic donor, obtained by the method of complex formation with different acceptors, agree well with one another, although the acceptors used differ considerably in their strength and in the nature of the interaction; the halides of group III metals[19,93,146] and carboxylic acids[94,149] were studied.

An unsatisfactory feature of this approach is that inductive and steric effects are underestimated. More accurate values of the energy of $p\pi$-conjugation (E_c) can be obtained using correlation equations relating the values of $-\Delta H$ to the sum of the induction ($\Sigma\sigma^*$) and steric (ΣE_s^0) constants of the substituents on the heteroatom of the donor. An equation of this kind has been obtained[147] for complexes of gallium trichloride with a number of aliphatic ethers containing substituents with markedly different induction and steric constants. Using this equation, it is possible to calculate the value of $(-\Delta H)_{calc}$ for an aromatic ether in accordance with the values of $\Sigma\sigma^*$ and ΣE_s^0, and the energy of $p\pi$-conjugation for the ether can be determined as the difference $E_c = (-\Delta H)_{calc} - (-\Delta H)_{expt}$. This method of determining E_c is independent of the linear relationship (1), and is essentially a second, independent method of determining E_c from data on the heats of formation of the complexes.

In the determination of E_c by this method it is important to estimate correctly the values of σ^* and E_s^0 for the phenyl substituent. The induction constant of the phenyl substituent is +0.6,[152] but the choice of the steric constant is more complicated. Because of the marked difference in the dimensions of the phenyl group in the plane of the ring and at right angles to it, two steric constants are given for this substituent ($E_s^0 = -0.3$ and -2.77 [147,153]). In complexes in which the $p\pi$-conjugation is broken down, the ring occupies the most favourable position from the viewpoint of steric conditions. For example, in the complex $C_6H_5OCH_3.AlBr_3$, the plane of the ring is perpendicular to the COC plane.[150] The low value of the steric constant $E_s^0 = -0.3$ apparently reflects fairly objectively the steric influence of the phenyl substituent in this complex. The same value of E_s^0 for the phenyl substituent was used[147] to calculate the energy of the $p\pi$-conjugation of aromatic phosphines. This estimate of E_s^0 is confirmed by Tolman's data[74] on the steric effects of phosphine-containing ligands. The steric effects of trimethylphosphine and dimethylphenylphosphine practically coincide, and the steric properties of triphenylphosphine are similar to those of tertiary aliphatic phosphines containing alkyl groups not branched in the α-position.

Since the steric constants of the phenyl substituent and alkyl substituents with the normal structure are similar, steric effects have relatively little influence on the magnitude of $\Delta\Delta H$. The main contribution to the value of $\Delta\Delta H$, in addition to the energy of $p\pi$-conjugation, is made by the difference in the energies of the donor–acceptor bonds due to the difference in the inductive effects of the alkyl and phenyl substituents. This error can be taken into account by introducing into the value of $\Delta\Delta H$ a correction for the inductive effect of the phenyl substituent equal on the average to 1.2 kcal mole^{-1} per ring.[147] The values of E_c for aromatic ethers, sulphides, amines, and phosphines, obtained using the correlation equations, E_c(I), and from the values of $\Delta\Delta H$ with a correction for the inductive effect of the aryl fragments, E_c(II), are analysed below (see Tables 6 and 7).

The introduction of two *ortho*-substituents leads to the production of appreciable steric hindrance to intermolecular donor–acceptor interaction in $AlBr_3$ complexes. Thus the heat of the addition of $AlBr_3$ molecules to dimethoxydurene (21.2 kcal mole^{-1})[88] is lower than that to aliphatic ethers (23.3 kcal mole^{-1}), although the $p\pi$-conjugation in dimethoxydurene is prevented by steric factors (see above). At the same time, in the complexes of aromatic phosphines with trifluoroacetic acid, the influence of *ortho*-substituents on the strength of the donor–acceptor bond is slight, because of the low sensitivity of the H-bond to steric effects. Thus the heats of formation of the complexes $Alk_3P.(CF_3COOH)_2$ in benzene are on the average 27.5 kcal mole^{-1},[149] whereas that for the corresponding complex of diethylmesitylphosphine is 27.3 kcal mole^{-1}. Thus the energy of $p\pi$-conjugation in the diethylmesitylphosphine molecule is zero, in agreement with the electronic spectra (see below), which indicate that there is steric inhibition of $p\pi$-conjugation in this compound. The heats of formation of the complexes of trifluoroacetic acid with triphenylphosphine (18.4 kcal mole^{-1}) and diethylphenylphosphine (24.6 kcal mol^{-1}) are much lower, because of the expenditure of energy in the breakdown of $p\pi$-conjugation on complex formation.

IV. THE ESTIMATION OF THE DEGREE OF $p\pi$-CONJUGATION

Many physicochemical properties of aromatic compounds of group V and VI elements can be interpreted in terms of the conjugation of the UEP of the heteroatom with the π-electron system of the aromatic fragment. At the present stage of development, some physicochemical methods for studying molecules make possible only comparative estimates of the degree of $p\pi$-conjugation in compounds with similar compositions and structures (UV, NMR, and Raman spectroscopy). Other methods, such as PES, make it possible to characterise quantitatively the degree of $p\pi$-conjugation in certain compounds. The most reliable information on the energy of $p\pi$-conjugation is given by methods involving the measurement of thermal effects such as heats of combustion and the calorimetric study of the electron-donor properties of the corresponding compounds. The results of the study of $p\pi$-conjugated systems by some of these methods can be considered.

1. Electronic Spectra

The interaction of the UEP of a heteroatom with a neighbouring π-system can be regarded as an intramolecular donor–acceptor interaction.[1,2] The electronic spectra of aromatic compounds containing a heteroatom should contain intense bands similar in character to the charge-transfer bands of intermolecular charge-transfer complexes. A necessary condition for the appearance of charge-transfer

bands is the overlap of the orbitals of the donor and acceptor in the ground state,[2] or, in the case of aromatic compounds, the overlap of the orbital of the UEP of the heteroatom and the π-system of the aromatic fragment. The conditions of orbital overlap and hence the spectral manifestation of $p\pi$-conjugation are determined to a large extent by the geometry of the molecules.

When there is steric inhibition of the $p\pi$-conjugation in aromatic amines[95] and ethers,[156,157] the spectra of the compounds, in which there is no conjugation, are similar to the spectra of the corresponding aromatic hydrocarbons. For example, in the case of benzoquinuclidine, the orbital of the UEP of the nitrogen atom is orthogonal to the orbitals of the π-system of the aromatic fragment, and the electronic absorption spectrum is similar to that of benzene.[158] The spectrum of dimethoxydurene, in the molecule of which the planes of the methoxy-groups are perpendicular to the plane of the ring (compound (XXVII) in Table 1), is similar to the spectrum of durene.[88] The influence of steric inhibition of $p\pi$-conjugation on the electronic spectra of aromatic sulphides has also been extensively studied,[26,27,157,159,160] but in contrast to the case of amines and ethers, even those aromatic sulphides showing the greatest degree of steric overcrowding absorb more strongly in the near ultraviolet than the corresponding aromatic hydrocarbons.

The nature of the electronic spectra of aromatic phosphines has been discussed for many years (see Refs. 6 and 161–164 and references therein). Recent studies[26,31,165,166] have shown that the electronic spectra of dialkylarylphosphines undergo considerable changes with increase in the volume of the alkyl group or on the introduction of bulky *ortho*-substituents (Table 5). Thus as in the case of aromatic amines, ethers, and sulphides, the nature of the electronic spectra of aromatic phosphines depends on the degree of overlap of the UEP of the phosphorus atom with the orbitals of the π-system, that is on the degree of $p\pi$-conjugation.

Table 5. Parameters of the long-wave band in the ultraviolet spectra of dialkylarylphosphines.

Phosphine	λ_{max}, nm	$10^{-3}\,\varepsilon$	$10^{2}f$	Refs.
$C_6H_5P(CH_3)_2$	251	5.6	13.0	[165]
$C_6H_5P(C_2H_5)_2$	255	3.3	7.5	[163]
$C_6H_5P(C_4H_9)_2$	256	3.0	7.3	[163]
$C_6H_5P(C_4H_9\text{-iso})_2$	257	2.4	5.9	[163]
$C_6H_5P(C_5H_7\text{-iso})_2$	259	2.0	5.6	[163]
$C_6H_5P(C_4H_9\text{-t})_2$	260	1.7	4.7	[165]
$4\text{-}CH_3C_6H_4P(CH_3)_2$	253	3.6	—	[166]
$2\text{-}CH_3C_6H_4P(CH_3)_2$	254	4.8	—	[166]
$2,4,6\text{-}(CH_3)_3C_6H_2P(CH_3)_2$	265	2.3	—	[166]
$2,4,6\text{-}(CH_3)_3C_6H_2P(C_2H_5)_2$	260	1.7	—	[161]

Symbols: ε is the molar absorptivity, and f the oscillator strength.

The high sensitivity of the electronic spectra to $p\pi$-conjugation makes it possible to detect this effect not only in aromatic sulphides and phosphines but also in the compounds of the elements of later periods,[30,167,168] although the conditions of overlap of the orbital of the UEP with the π-system become less favourable with increase in the atomic number of the heteroatom. For example, it has been shown[30] that as in the case of the compounds of oxygen and sulphur, the intensity of absorption by aromatic compounds of selenium C_6H_5SeR in the near ultraviolet decreases with increase in the volume of the aliphatic group R. The changes in the electronic spectra with change in temperature are characteristic not only of the aromatic sulphides and phosphines,[27,31,168] but also of the triaryl derivatives of arsenic, antimony, and bismuth.[168] This effect is usually attributed to the presence of conjugated and non-conjugated conformers in solution and to the displacement of the conformational equilibrium with change in temperature.

Thus the steric inhibition of $p\pi$-conjugation is clearly revealed in the electronic spectra, and this makes it possible to establish in narrow series of compounds the relationship between the spectral characteristics and the geometry of the molecules. Quantitative estimates of the degree of $p\pi$-conjugation cannot usually be obtained, however, from spectrophotometric data, particularly when the spectra of compounds with different heteroatoms are compared.[169,170]

One of the main reasons for these difficulties is apparently that for a fairly wide range of $p\pi$-conjugated molecules there is no unique dependence of the parameters of the intramolecular charge-transfer bands on the energy of $p\pi$-conjugation. To continue the parallel between $p\pi$-conjugation and intermolecular donor–acceptor interaction, it may be stated that the relationship between the position and intensity of the charge-transfer bands and the thermodynamic parameters of the complexes is extremely complicated.[1,93,171]

In the comparison of the electronic spectra of aromatic compounds of the elements of periods II and III, it is necessary to take into account not only the effect of $p\pi$-conjugation but also the possible contribution of the *d*-orbitals of the sulphur and phosphorus atoms to the MO of aromatic sulphides and phosphines. Although the concept of unoccupied *d*-orbitals has been criticised,[172,173] it is still widely used,[145,174] and provides a simple and natural explanation of the above differences in the spectral behaviour of the compounds of elements of periods II and III when there is steric inhibition of $p\pi$-conjugation.

It should also be noted that the electronic spectra are integral characteristics of the compounds, and result from the superposition of individual bands. Information on the number of bands and their parameters is necessary for a correct assignment of the bands and the correct comparison of experimental data with quantum-chemical calculations. The integral absorption curve can be described by a set of Gaussians.[154,155,175–177] Most frequently, however, the number of bands is estimated from the number of clearly defined maxima, and bands appearing as shoulders are taken into account or ignored arbitrarily. The problem of distinguishing the bands becomes particularly acute for systems in which there is an equilibrium between conjugated and non-conjugated conformers whose electronic spectra differ considerably.

The breakdown of $p\pi$-conjugation is clearly reflected in the nature of the change in the spectrum on going from an aromatic compound containing a heteroatom to a complex with a strong electron acceptor. The spectra of the complexes of aromatic amines and ethers with the halides of group III metals and strong carboxylic acids are similar to the spectra of the corresponding aromatic hydrocarbons.[93,94,146,178,179] Similar changes in the electronic spectra take place when aromatic amines are protonated.[95] Since the groups OCH_3, MX_3 and $N(CH_3)_2.MX_3$ have strong inductive ($-I$) effects,[150] the inductive effect of the substituent apparently does not influence the parameters of the long-wave band of the aromatic fragment.

The spectra of aromatic sulphides also change considerably when they form complexes with the halides of group III metals, but in contrast to the complexes of amines and ethers, the complexes of aromatic sulphides absorb much more strongly than the corresponding hydrocarbons. Thus the spectrum of the complex $(C_6H_5)_2S.GaCl_3$ is similar to the

spectrum of diphenyl sulphoxide, and not to the spectrum of benzene.[179] A similar picture is observed when aromatic phosphines form complexes with strong electron acceptors[19] or are protonated.[166] The spectra of these systems differ considerably from those of the corresponding hydrocarbons. The spectrum of a solution of triphenylphosphine in trifluoroacetic acid is similar to the spectrum of triphenylphosphine oxide.[19] These facts agree with the view that the 3*d*-orbitals of the phosphorus and sulphur atoms take part in the formation of the MO of aromatic sulphides and phosphines.

The analogous changes taking place in the electronic spectra of aromatic compounds containing a heteroatom when the UEP of the heteroatom forms an intermolecular donor–acceptor bond on the one hand and when bulky substituents are introduced on the other hand leaves no doubt that the intense absorption in the long-wave range of the electronic spectra of these compounds is related to the interaction of the UEP of the heteroatom with the neighbouring π-system, that is to $p\pi$-conjugation. The spectral manifestation of the breakdown of the $p\pi$-conjugation in aromatic compounds containing a heteroatom when complexes are formed has provided a basis for developing a method for estimating the energy of $p\pi$-conjugation.[93,146]

2. NMR Spectroscopy

The parameters of the NMR spectra, namely the chemical shifts (δ) and the spin–spin coupling constants (J), show a complex dependence on the structural characteristics of molecules and reflect the influence of various factors (inductive, resonance, steric) on the state of individual fragments of the molecules. Nevertheless, in spite of the fact that the parameters of the NMR spectra depend on many factors, they have been widely used to study the effects of $p\pi$-conjugation. Systematic studies of $p\pi$-conjugation by NMR in aromatic and unsaturated compounds of group VI elements have been described in Refs. 26, 31, 180–189 and references therein.

Comprehensive studies of alkyl phenyl ethers[181,185,187] and sulphides[181,186] showed that the most informative parameters for estimating the effects of $p\pi$-conjugation by NMR are those relating to the atom in position 4 of the phenyl ring. This position in the molecule is less influenced than other positions by the inductive and steric effects of the ER group. The values of $\delta(^{13}C_n)$ for compounds of the type C_6H_5ER are (p.p.m.):

R	O (Ref.187)	S (Ref.186)	Se (Ref.182)	CH_2 (Ref.181)
CH_3	120.92	125.06	125.55	125.67
C_2H_5	120.57	125.74	126.24	125.67
C_3H_7	120.25	125.68	126.16	125.58
iso-C_3H_7	120.55	126.72	126.84	125.62
t-C_4H_9	123.27	128.57	128.10	125.63

Since the value of $\delta(^{13}C)$ is directly related to the electron density on the carbon atom, it follows in accordance with the induction constants of the ECH_3 groups that a decrease in the shielding of the C_n atom in the compounds studied should be expected, compared with benzene ($\delta(^{13}C)$ = 128.70 p.p.m.) or ethylbenzene ($\delta(^{13}C_n)$ = 125.67 p.p.m.). The increase in the degree of shielding of the C_n atoms of the compounds studied is a consequence of the $p\pi$-conjugation of the UEP of the heteroatoms with the π-system. Comparison of the values of $\delta(^{13}C_n)$ for R = CH_3 indicates that the degree of $p\pi$-conjugation decreases in the order $C_6H_5OCH_3 > C_6H_5SCH_3 > C_6H_5SeCH_3$. The nature of the changes in $\delta(^{13}C_n)$ with increase in the size of R reflects the influence of steric effects on $p\pi$-conjugation. The chemical shifts $\delta(^{13}C_n)$ of alkylbenzenes are practically the same for all compounds.

For the oxygen compounds there is a sharp decrease in the shielding only for R = $C(CH_3)_3$. For phenyl alkyl sulphides and selenides, the shielding decreases regularly in the order C_3H_7 > iso-C_3H_7 > t-C_4H_9.

The main reason for the observed regularities is the steric inhibition of $p\pi$-conjugation. This is indicated by the good correlation between the values of $\delta(^{13}C_n)$ and the steric constants $E_s^0(CH_2R)$ of the substituents for phenyl alkyl sulphides[181] and phenyl alkyl selenides.[182] Proof that the observed changes in $\delta(^{13}C_n)$ are due to steric factors is provided by the fact that, in contrast to the phenyl derivatives, in compounds of the mesityl series, for example in mesityl alkyl sulphides,[184] the value of $\delta(^{13}C_n)$ remains constant for all R (CH_3, C_2H_5, iso-C_3H_7, t-C_4H_9), since in these compounds the $p\pi$-conjugation is prevented by steric factors.

Thus according to the NMR data, the intensity of the $p\pi$-conjugation in alkyl phenyl compounds of group VI elements is determined to a large extent by the conformation of the molecules, which depends on the volume of the alkyl group. This conclusion is confirmed by the results of a study of the chemical shifts of the signal of the proton in position 4 and by the changes in $J(^1H-^1H)$ and $J(^{13}C-^1H)$ for phenyl alkyl ethers and sulphides.[185–187] A similar conclusion that there is steric inhibition of conjugation was reached on the basis of ^{13}C and ^1H NMR data for the β-atoms of the vinyl group in alkyl vinyl ethers and sulphides.[180,183,190]

The magnitude of the chemical shift of the ^{17}O signal is extremely sensitive to the effects of $p\pi$-conjugation in aromatic and unsaturated oxygen-containing compounds. The ^{17}O NMR data for these compounds[189] confirmed the conclusions reached from the ^{13}C and ^1H NMR data. It was shown that the $p\pi$-interaction between the UEP of the oxygen atom and the aromatic (unsaturated) fragment remains approximately the same for R = CH_3, C_2H_5, and iso-C_3H_7, and changes sharply on going to t-C_4H_9.

For aromatic compounds of the group V elements, the NMR studies of $p\pi$-conjugation have been less systematic, and the results are less unambiguous. It has been pointed out[191] that it is difficult to interpret the spectral data, since the NMR spectra of these compounds may be influenced by many different factors. From an analysis of the relationship between $\delta[^{13}C(R^{13}CH_3)]$ and $\delta[^{31}P(R^{31}PPh_2)]$ it was concluded that there is only slight overlap of the orbital of the UEP of the phosphorus atom and the π-system of aryl phosphines.[192] In Ref. 193 it was shown that triarylphosphines show a common correlation with alkylphosphines between $\delta(^{31}P)$ and θ (where θ is the valence angle of the phosphorus atom). Assuming that the inductive influence of the substituents on the magnitude of $\delta(^{13}C)$ in the *para*- and *meta*-positions of monosubstituted benzenes are approximately the same, the authors of a number of studies[192,194] took as a measure of the resonance effects the quantity $\Delta\delta = \delta(^{13}C_n) - \delta(^{13}C_m)$. Analysis of the values of $\Delta\delta$ for arylphosphines[192,194–196] led to the conclusion that there is little $p\pi$-conjugation. According to Ref. 192, the value of $\Delta\delta$ is 0.5 p.p.m. for arylphosphines and 12.5 p.p.m. for dimethylaniline. ^{13}C NMR data indicating a marked difference in the ability of N and P atoms to undergo $p\pi$-conjugation have been reported.[197]

At the same time, the results of a study of the anisotropy of the chemical shift of the ^{31}P NMR signal for trimethyl- and triphenylphosphines in the liquid-crystal phase have been interpreted[198] in terms of the delocalisation of the UEP of the phosphorus atom in triphenylphosphine. The same conclusion was reached from a study of $J(^{31}P-^1H)$ for phenylphosphines.[199] An analysis of the temperature dependence of the difference $\delta(^{31}C_n) - \delta(^{31}C_m)$ for aromatic phosphines $C_6H_5PR_2$ and sulphides C_6H_5SR for R = CH_3, C_2H_5, iso-C_3H_7, and t-C_4H_9 indicates[26,31] that in solution there is an equi-

librium between conjugated and non-conjugated conformers; the concentration of the non-conjugated conformer increases in the R order given. In the case of the planar conformation, the maximum contribution of the UEP of the phosphorus atom to the $p\pi$-conjugation with the ring is ~50% of the contribution of the UEP of the nitrogen atom in dimethylaniline.

3. Photoelectron Spectroscopy

Photoelectron spectroscopy (PES) is an extremely promising method for studying intramolecular interactions.[200] When combined with quantum-chemical calculations, this method makes it possible to characterise quantitatively the energies of the MO of the molecules and to assign the bands in the PES. The application of this method to organic and heteroorganic compounds has been examined in general reviews[200,201] and also in special reviews on the PES of phosphorus compounds,[202,203] the PES of oxygen and sulphur compounds,[204] and the use of PES to study the conformations of molecules.[205]

The parametrisation of quantum-chemical calculations from PES data is widely used in the study of the regular features of the production of MO. In particular, for aromatic compounds of group VI elements of the type $C_6H_5ECH_3$, the contribution of the UEP of the heteroatom to the HOMO has been determined, and it has been shown that the energy of the HOMO calculated by the simple MO method agrees well with the experimentally determined value.[30,124] The regular features of the influence of the size of the aliphatic group R in series of compounds of the type C_6H_5ER on the conformation of the molecules have been determined.[3,30] It has been shown that in disubstituted benzenes with two electron-donor substituents, the greater contribution to the HOMO is made by the substituent with the lower IP.[206] The conditions for steric inhibition of $p\pi$-conjugation in substituted benzenes have been determined.[207,208] It has been shown for the case of compounds of group VI elements that PES combined with quantum-chemical calculations makes it possible to reach conclusions about the three-dimensional structure of molecules.[209]

A number of papers[202,210-216] have described the geometry and $p\pi$-conjugation of compounds of phosphorus and other group V elements. It has been established that IP_1 is linearly dependent on the valence angle of the heteroatom in the phosphine series,[18] and also in more extensive series of compounds of group V elements.[210] In the estimation of the extent of $p\pi$-conjugation in aromatic phosphines, it was first concluded from the interpretation of the PES that there is practically no $p\pi$-conjugation or that it is negligible.[211-213] Later more detailed PES studies and quantum-chemical calculations led to the conclusion that the UEP of the phosphorus atom makes a significant contribution to the HOMO of phenylphosphine and other aromatic phosphines.[164,214,216]

There are a number of different approaches in the use of PES to estimate the extent to which the UEP of the heteroatom is combined with the π-system. In certain series of compounds, a relative characteristic of the extent of $p\pi$-interaction can be obtained by comparing the values of the resonance integrals β_{E-C} calculated from PES data.[217] This parameter has been used to estimate the degree of binding of the UEP in compounds of the type C_6H_5OR and in isologues of anisole,[3,5,218] and in a comparison of the effects of $p\pi$-conjugation in non-substituted and perfluorinated thiophenols, thioanisoles, and diphenyl sulphides.[219]

In accordance with the scheme given in the Figure, the relative efficiency of $p\pi$-interaction has been characterised[219-221] using the difference in the energies of the HOMO (π_1) and the levels π_2 or π_3: $\Delta_{1,2} = \pi_1 - \pi_2$ or $\Delta_{1,3} = \pi_1 - \pi_3$; both quantities can be estimated from the PES. The parameter $\Delta_{1,3}$ can also be obtained from the X-ray fluorescence spectra.[221] The numerical values of $\Delta_{1,2}$ and $\Delta_{1,3}$ have been used to estimate the degree of $p\pi$-interaction and the conformations of the molecules of diphenyl sulphide and other sulphur compounds,[220] aryl alkyl and diaryl sulphides and their perfluorinated analogues,[219,220] and various phosphines.[202]

The PES is influenced considerably, however, not only by $p\pi$-conjugation but also by other factors such as the inductive and steric influence of the substituents, hyperconjugation, $p_\pi-d_\pi$ conjugation, etc. Thus the approach described above is useful for comparing the effects of $p\pi$-conjugation in series of compounds with similar compositions and structures.

In addition to PES, X-ray electron spectroscopy (XES) is extremely promising for the analysis of $p\pi$-conjugation. It has been suggested[222] that a measure of the binding of the UEP in a compound being studied is provided by the quantity $\Delta = IP - IP_{stand} - 0.8(E_i - E_{i(stand)})$, where IP and IP_{stand} are the ionisation potentials (determined from the PES), and E_i and $E_{i(stand)}$ are the binding energies of the internal electrons of the heteroatom (determined from the PES) for the compound being studied and a compound taken as standard respectively. A positive value of Δ corresponds to bonding character for the UEP, and a negative value corresponds to antibonding character. The combined analysis of the ionisation potentials of the outer and inner electrons of the $p\pi$-conjugated molecule being studied and the molecule of the standard compound, in which the UEP of the heteroatom is not combined, makes it possible to eliminate the influence of differences in the charges of the atoms and other electronic effects.

The values of Δ have been determined for a number of $p\pi$-conjugated molecules. It has been shown that in aliphatic amines, the UEP of the nitrogen atom has antibonding character (for trimethylamine $\Delta = -0.9$ eV), and this has been attributed to the repulsion of the UEP by the electrons of the C–H bonds. On the other hand, for the aniline molecule, $\Delta = 1.3$ eV, indicating that the UEP of the nitrogen atom is combined to a considerable extent with the π-system. Similarly, the UEP of the oxygen atom of dimethyl ether ($\Delta = -1.8$ eV) is antibonding, whereas in the phenol molecule ($\Delta = 0.7$ eV) it is combined with the π-system of the ring.

Thus the combined use of PES and XES makes it possible to estimate quantitatively the effects of $p\pi$-conjugation.

4. The Energy of $p\pi$-Conjugation from Thermochemical Data

Like any interaction, $p\pi$-conjugation is characterised quantitatively by its energy. At the present time, the energy of $p\pi$-conjugation is determined by two thermochemical methods: a method based on the measurements of heats of combustion, and the recently developed method of complex formation. The first method has been known for a long time, but the data obtained by this method are extremely contradictory;[93,146,173] there have been no systematic studies of aromatic compounds containing a heteroatom, apart from work[223] on the measurement of the heats of combustion of a series of alkyl and aryl vinyl ethers $H_2C{=}CHOR$ and the determination (with a correction for the inductive effect) of the values of the energies of $p\pi$-conjugation E_c (kcal mole^{-1}) of the following compounds:

R	C_2H_5	C_3H_7	iso-C_3H_7	C_4H_9	C_2H_4Cl	C_6H_5	$H_2C{=}CH$
E_c	6.8	6.8	6.5	7.3	7.3	6.6	10.1

In Refs. 223 and 224, the MINDO/2 method gave estimates of E_c agreeing with experimental data. The method of determining E_c from heats of combustion has much in common with the method of complex formation, the principles of which were described above; the values of E_c obtained are given in Tables 6 and 7. Both methods are based on the comparison of the thermochemical properties of aromatic and corresponding aliphatic compounds with allowance (in recent studies) for the differences in the inductive effects of the corresponding groups on the heteroatom.

Table 6. Values of the energy of $p\pi$-conjugation (kcal mole^{-1}).*

Compound	E_c (I)	E_c (II)
$C_6H_5OCH_3$	6.2	6.2
$C_6H_5OC_2H_5$	4.8	5.5
$(C_6H_5)_2O$	8.8	8.6
$C_6H_5SCH_3$	—	3.7
$C_6H_5SC_2H_5$	—	2.7
$(C_6H_5)_2S$	—	5.5
$C_6H_5N(CH_3)_2$	—	8.4
$(C_6H_5)_2NCH_3$	—	14.6
$C_6H_5P(C_2H_5)_2$	5.2	3.0
$(C_6H_5)_2PC_2H_5$	—	4.9
$(C_6H_5)_3P$	7.1	6.9
$(4\text{-}CH_3C_6H_4)_3P$	—	4.9
$2,4,6\text{-}(CH_3)_3C_6H_2P(C_2H_5)_2$	—	~0

*The values of E_c(I) were obtained using the correlation equations, with the acceptor $GaCl_3$;[147] the values of E_c(II) were obtained from the values of $\Delta\Delta H$ [19,94,146,149,150] with a correction for the inductive effect of the aryl ring, the acceptors were metal halides and carboxylic acids, and the average values are given.

Table 7. Values of the energy of $p\pi$-conjugation for aromatic ethers (kcal mole^{-1}).*

Compound	E_c (I)	E_c (II)	Compound	E_c (I)	E_c (II)
$C_6H_5OCH_3$	6.2	6.2	$1,4\text{-}(CH_3O)_2C_6(CH_3)_4$	—	0
$3\text{-}CH_3C_6H_4OCH_3$	5.8	5.5	$C_6H_5OC_2H_5$	4.8	5.3
$4\text{-}CH_3C_6H_4OCH_3$	5.4	5.3	$(C_6H_5)_2O$	8.8	8.9
$3,5\text{-}(CH_3)_2C_6H_3OCH_3$	—	5.3	$3\text{-}CH_3C_6H_4OC_6H_5$	—	8.9
$2,6\text{-}(CH_3)_2C_6H_3OCH_3$	—	0.6	$4\text{-}CH_3C_6H_4OC_6H_5$	—	8.9
$3\text{-}BrC_6H_4OCH_3$	6.8	6.9	$(4\text{-}CH_3C_6H_4)_2O$	—	8.3
$4\text{-}BrC_6H_4OCH_3$	6.4	6.5	$(4\text{-}BrC_6H_4OC_6H_5)$	—	9.4
$1,2\text{-}(CH_3O)_2C_6H_4$	—	9.1	$(4\text{-}BrC_6H_4)_2O$	—	10.5
$1,3\text{-}(CH_3O)_2C_6H_4$	—	15.9	$4\text{-}CH_3OC_6H_4OC_6H_5$	—	19.5
$1,4\text{-}(CH_3O)_2C_6H_4$	—	12.8	$4\text{-}CH_3OC_6H_4OC_6H_4Br\text{-}4$	—	19.6

*The values of E_c(I) were obtained by the method of complex formation using correlation equations, with $GaCl_3$ as the acceptor;[147] the values of E_c(II) were obtained from the values of $\Delta\Delta H$ [88,90,150,151] with a correction for the inductive effect of the aryl ring, with $AlBr_3$ and $GaCl_3$ as the acceptors.

The values of E_c(I) and E_c(II) (Tables 6 and 7), obtained by measuring the heats of complex formation by two independent methods (see section III), are similar to one another. The values of E_c for the compounds studied vary over a wide range (0–20 kcal mole^{-1}), depending on the nature of the heteroatom and the substituents, the steric conditions, etc. In a series of analogous compounds (Table 6), the heteroatoms can be arranged in the following order of decreasing ability to take part in $p\pi$-conjugation: N > O > S ≅ P. The energy of $p\pi$-conjugation for aromatic amines is approximately three times that for the corresponding phosphines.

The effects of the steric inhibition of $p\pi$-conjugation in aromatic ethers, revealed in the UV, NMR, and PE spectra, are characterised quantitatively by the data in Table 7. The energy of $p\pi$-conjugation for anisole is fairly high (6.2 kcal mole^{-1}). The introduction of two CH_3 groups in the 2,6-positions of the phenyl ring removes the methoxy-group from the conjugation; E_c for 2,6-dimethylanisole is only 0.6 kcal mole^{-1}. The effect of the steric inhibition of $p\pi$-conjugation is revealed by comparing the values of E_c for 1,4-dimethoxybenzene (12.8 kcal mole^{-1}) and dimethoxydurene (~0). A similar picture is observed for aromatic phosphines (Table 6). In diethylmesitylphosphine, the $p\pi$-conjugation is destroyed for steric reasons, and accordingly $E_c \cong 0$, whereas E_c for diethylphenylphosphine is 3–5 kcal mole^{-1}, and that for triphenylphosphine is ~7 kcal mole^{-1}.

The introduction of the electron-donor CH_3 group in the 2-, 3-, or 4-position or of two CH_3 groups in the 3,5-positions of the phenyl ring of anisole leads to a decrease in the energy of the $p\pi$-conjugation of the UEP of the oxygen atom with the ring. On the other hand, electron-acceptor substituents (the Br atom) lead to an increase in E_c (Table 7).[88,150,151]

An interesting feature is that the introduction of a CH_3 group into the 3- or 4-position of one of the rings of diphenyl ether, in contrast to anisole) is not accompanied by a decrease in the energy of $p\pi$-conjugation (Table 7). In these compounds, a conformation ensuring $p\pi$-conjugation of the UEP of the oxygen atom with the π-system of the non-substituted ring is produced (see above). Electron-acceptor substituents (for example Br) lead to better overlap of the UEP of the oxygen atom with the π-system of the substituted ring and to less effective overlap with the non-substituted ring. In accordance with this, the value of E_c for $4\text{-}BrC_6H_4OC_6H_5$ is greater than that for diphenyl ether. The question of the energy of $p\pi$-conjugation and the conformation of diphenyl ethers with different substituents (CH_3, Br, OCH_3, OC_6H_5) has been examined.[151]

The values of E_c for *ortho*-, *meta*-, and *para*-dimethoxybenzene, given in Table 2, represent the total energy of conjugation of two methoxy-groups. The energy of the $p\pi$-conjugation of *para*-dimethoxybenzene is slightly less than that of *meta*-dimethoxybenzene, because of the "saturation" effect.[88,152] The energy of conjugation of *ortho*-dimethoxybenzene is even lower,[90] apparently because one of the methoxy-groups is not coplanar with the ring (see above).

Continuing the parallel between $p\pi$-conjugation and intermolecular donor–acceptor interaction, it should be noted that the significance of the value of E_c determined by thermochemical methods corresponds to the enthalpy of formation of the complex ($-\Delta H_c$), which in addition to the energy of the donor–acceptor bond ($-\Delta H_{DA}$) also contains a contribution from the energy of the rearrangement of the molecules of the donor and the acceptor on complex formation. Similarly, the energy of $p\pi$-conjugation (E_c), in addition to the energy of the π-bond between the heteroatom and the π-system, contains a contribution associated with the differences in the geometries of the aromatic and aliphatic molecules, for example a contribution associated with the difference in the steric interactions.[225] On complex formation with strong electron acceptors, these differences in the geometries, which are most clearly defined in the case of amines, are levelled out. In the determination of the energy of the $p\pi$-conjugation of strained molecules by the method of complex formation, it must be borne in mind that complex formation may

lead to a change in the strain energy, and this will be reflected in the $\Delta\Delta H$ values. This situation has been described[90] for the complexes of cyclic alkylaromatic diethers. The energy of $p\pi$-conjugation of benzo-1,4-dioxan was found to be much too high, since the value of $\Delta\Delta H$ contains a contribution from the change in the strain energy and the conformational rearrangement of the heterocycle.

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The above data indicate fairly reliably that there is intramolecular $p\pi$-interaction not only in aromatic compounds of nitrogen, oxygen, and sulphur, but also in compounds of the heavier elements of groups V and VI, and particularly in phosphorus compounds. The problem of $p\pi$-conjugation in phosphorus compounds has been widely discussed.[6,19,31,161-166,226,227] The use of accurate and sensitive methods will apparently make it possible to find new hetero-organic compounds in which $p\pi$-interaction with an aromatic system may take place.

While the present review was being prepared for publication, new reviews[228,229] and original papers on the geometry of $p\pi$-conjugated molecules[230-233] and the study of $p\pi$-conjugation by electron spectroscopy, NMR, PES, quantum-chemical methods, etc.[234-240] were published.

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