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Ionisation Potentials of Aromatic and Heterocyclic Compounds

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The relation between the ionisation potentials of aromatic and heterocyclic compounds and their electronic structures is considered. The nature of the orbitals in the ground states of molecules of different structures is examined on the basis of an analysis of the ionisation potentials. It has been shown how substituents affect the positions of the electronic levels of aromatic compounds.
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I. INTRODUCTION

During recent years, there has been an increase in the number of studies on the photoionisation of organic compounds in the gas phase, dealing with the investigation of the electronic structure of molecules and the mechanism of their decomposition on ionisation. The advances achieved in this field are due to the successful development of the technique of the accurate determination of adiabatic ionisation potentials (i.p.) by the photoionisation method.

At the present time this method has been developed and used to determine ionisation potentials by Soviet and non-Soviet investigators[1-9]. Valuable information about the upper ionisation potentials of aromatic compounds was obtained by photoelectronic spectroscopy[10-12].

The ionisation potentials of a large number of aromatic and heterocyclic compounds containing $\rangle N-$, $\rangle C=O$, $-O-$, and $-S-$ groups in different positions are now known. However, this information has not been arranged systematically, which makes it difficult to discover the characteristic properties of the structures of organic compounds.

From the standpoint of electronic structures and the influence of chromophoric groups and substituents on the π-electron system, aromatic compounds can be usefully divided in three main groups.

1. Aromatic-hydrocarbons with an upper π-electron level in the ground state.

2. Aromatic compounds in which the heteroatoms supply a lone pair of p electrons to the π-electron system: (a) compounds with a chromophoric group outside the ring (aniline, phenol, and others); (b) heterocyclic compounds containing the $-N\langle$, $-O-$, and $-S-$ groups (pyrrole, furan, and others).

3. Aromatic compounds in which each heteroatom supplies one p electron to the π-electron system: (a) nitrogen-containing heterocyclic compounds (pyridine and others); (b) aromatic compounds with a carbonyl group (quinones).

This classification of aromatic and heterocyclic compounds, based on an analysis of their ionisation potentials, provides information about the energies and the nature of their molecular and atomic orbitals.

This review deals with studies on the electronic structure of aromatic compounds of the above type on the basis of ionisation potentials, corresponding to the removal of electrons from different orbitals in the ground state, and the influence of substituents and heteroatoms on the nature and positions of π-orbitals.

II. IONISATION POTENTIALS OF AROMATIC HYDROCARBONS

The electronic structure of polycyclic aromatic hydrocarbons is characterised by a stable π-electron system ensuring a high energy stability of molecules of this type in photochemical and radiation-chemical reactions. Thus the mass spectra of benzene and naphthalene show a relatively low yield of fragment ions formed as a result of the disruption of the ring. The reactivity of aromatic polycyclic compounds in photochemical reactions is determined by the nature of their excited electronic states ($\pi\pi^*$). As a result of the delocalisation of electrons in the π orbitals of both the ground and excited electronic states, the valencies produced are common to the molecule as a whole, which determines the relative passivity of the ($\pi\pi^*$) states with respect to intermolecular interactions and the low photochemical activity of polycyclic hydrocarbons[13].

Accurate values of the first ionisation potentials for hydrocarbons were obtained by the photoionisation method mainly during the last few years (Table 1). The upper ionisation potentials corresponding to the energies of removal of electrons from various filled inner orbitals have been determined from the photoelectronic spectra of the molecules (Table 2).

The first ionisation potentials of polycyclic hydrocarbons (benzene, naphthalene, anthracene) decrease with the number of π electrons in the molecule, which is due to the decrease of the energy of the upper filled π orbital in consequence of the increase of the conjugation energy. It follows from the molecular orbital theory that the energy of the upper filled π orbital is linearly related to the first ionisation potential of the given molecule[1,14]. Accordingly, the first ionisation potential may be represented as follows:

$$I_p = -(\alpha + m_i\beta),$$

where α is the Coulombic integral, β the resonance integral, and m_i the coefficient of the energy of the ith molecular orbital. This equation has the specific form $I_p = 5.78 + 3.75\, m_i$ and holds satisfactorily for polycyclic hydrocarbons.

It has been shown[15] that the upper ionisation potentials of aromatic hydrocarbons and the energies of the filled π orbitals in the ground state are also correlated in the zeroth Hückel approximation.

Table 1. First ionisation potentials of aromatic hydrocarbons.

Compound	Ionisation potential, eV									
	photoionisation	Refs.	spectroscopy	Refs.	photoelectronic spectroscopy	Refs.	electron impact	Refs.	calc.	Refs.
Benzene	9.246±0.005	9	9.247	16	9.24	11				
o-Xylene	8.56±0.01	7	—	—	—	—	—	—	—	—
m-Xylene	8.57±0.01	7	—	—	—	—	—	—	—	—
p-Xylene	8.44±0.01	7								
Naphthalene	8.12±0.01	7	8.13	19.20	8.12	15	—	—	8.12	21
	8.14±0.02	18								
α-Methylnaphthalene	7.96±0.01	7	—	—	—	—	—	—	8.28	22
β-Methylnaphthalene	7.96±0.01	7	—	—	—	—	—	—	—	—
Anthracene	7.38±0.03	28								
	7.41	18	7.41	18	—	—	—	—	7.38	22
	7.3	23	—	—	—	—	—	—	7.3	24
Phenanthrene	7.75	18	7.69	18					7.96	25
									8.02	21
Azulene	7.41±0.01	18,26	7.41	18	7.42	15				
Indene			—	—	8.13	15	—	—	—	
Biphenylene			—	—	—	—	7.95±0.3	15	—	—
Biphenyl	8.27±0.01	7	—	—	—	—	—		—	—
p-Terphenyl			7.7	18						
Toluene	8.82±0.01	6	—	—	—	—	9.10	27	—	—
Diphenylmethane	—	—	—	—	—	—	8.95	27	—	—
Triphenylmethane	—	—	—	—	—	—	8.80	27	—	—
Naphthacene	6.88±0.03	28	—	—	—	—	—	—	—	—

Thus the following relation holds for the ionisation potentials and the π-orbital energies of benzene, indene, azulene, and biphenylene:

$$I_p^j = 6.22 + (2.77 \pm 0.15)\, m_j, \text{ eV},$$

where m_j is the coefficient of the energy of the jth π orbital in the ground state of the given molecule.

Table 2. The first and upper ionisation potentials of aromatic compounds.

Compound	Ionisation potential, eV				References
Benzene	9.24	11.48	14.0	16.83	11
Naphthalene	8.12	8.90	10.0	10.85	15
Indene	8.13	8.95	10.29	11.58	15
Azulene	7.42	8.49	9.91	10.85	15
Anthracene	7.41	9.25			18
Phenanthrene	7.75	9.35			18
Biphenyl	8.20	9.08	9.70	11.02	15

The resonance integral $\beta = 2.77 \pm 0.15$ eV is consistent with the estimate obtained from the ionisation potentials. This equation was used to estimate the ionisation potentials of the compounds investigated and showed good agreement with the experimental data in Table 2. Naturally, such an examination is important for the determination of the sequence and nature of the upper and lower π orbitals in the ground state of the given molecule.

The ionisation potentials of benzene were determined by El Sayed et al. from the ultraviolet absorption spectra on the basis of the convergence limits of the Rydberg series[16]. The first and second ionisation potentials, which are 9.247 and 11.489 eV, were attributed to the removal of electrons from π orbitals. The Rydberg series converging to 16.84 eV and representing a vibrational progression with a frequency of 900 cm^{-1} was attributed to the removal of an electron from the σ_{CC} orbital. The ionisation potentials of benzene determined from high-resolution photoelectronic spectra[11] agreed to a high degree of accuracy with the corresponding spectroscopic values (Fig. 1 and Table 2).

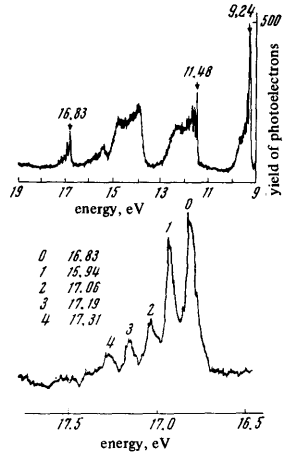


Figure 1. High-resolution photoelectronic spectrum of benzene.

The structure of the vibrational levels converging to the third ionisation potential also consists of a progression: 17.31, 17.19, 17.06, 16.94, and 16.83 eV. The results of these two investigations and also new studies on the photoionisation of benzene[4,5] (Fig. 2) established that the first and second ionisation potentials of benzene, 9.246 and 11.489 eV respectively, correspond to the energies of the removal of an electron from the π orbitals of the ground state and the ionisation potential of 16.83 eV corresponds to the removal of an electron from the σ_{CC} orbital. The photoionisation threshold at 14 eV (see the photoelectronic spectrum in Fig. 1) is probably also associated with the removal of an electron from the σ orbital, since according to the photoionisation data for benzene $C_6H_5^+$ fragment ions are formed at an energy of 13.8 eV.[5]

It should be noted that the calculation by the self-consistent field molecular orbital (SCF-MO) method for the benzene molecule[29] yielded unduly high energies for the upper σ_{1g} orbital. This is the reason for the incorrect assignment of the ionisation threshold associated with the removal of electrons from this σ orbital in a series of experimental studies on the ionisation potentials of benzene before the studies on the photoionisation[4,5] and photoelectronic spectra[11].

In the vicinity of the first ionisation potential the photoionisation curve for benzene shows breaks at energies of 9.33 ± 0.01 and 9.42 ± 0.01 eV, associated with the vibrational excitation of the second overtone of the ν_{18} symmetrical vibrations (670–690 cm^{-1}) of the molecular ion in the

Rydberg series converging to the first ionisation potential [5,30].

The ionisation potentials of anthracene and phenanthrene were determined from the electronic absorption spectra [18] on the basis of the convergence limits of the Rydberg series. The same workers determined by the photoionisation method the first ionisation potentials of naphthalene, anthracene, phenanthrene, and azulene, which agreed with the spectroscopic values. The photoionisation curves for anthracene and phenanthrene in Fig. 3 show that the vibrational excitation levels of the molecular ions observed in the vicinity of the first ionisation potentials are diffuse, which makes their assignment difficult.

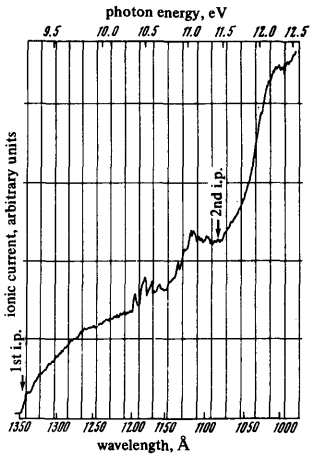


Figure 2. Photoionisation curve for benzene recorded on an MKh-1311 mass-spectrometer.

Absorption bands converging to the second ionisation potential have been observed on photoionisation curves between the first and second ionisation potentials of polycyclic hydrocarbons. The structure of the maxima is shown most distinctly for benzene in the energy range 10.4–11.2 eV (Fig. 2) (the first four maxima constitute a vibrational progression with a frequency of 0.09 eV), which can be accounted for by pre-ionisation from Rydberg molecular states, converging to the second ionisation potential of benzene corresponding to the removal of an electron from the π orbital $1b_1$ (a_{2u} level) [5]. The vibrational structure of the pre-ionisation bands of toluene is not resolved. The position of the first toluene band agrees with that of the first absorption band of toluene vapour due to the excitation of electrons from the lower π_1 orbital.

Pre-ionisation bands at energies of 9.1 and 9.0 eV converging to the second ionisation potentials of 9.25 and 9.35 eV have been observed for anthracene and phenanthrene [18]. It is noteworthy that the pre-ionisation levels of phenanthrene and azulene are of a pre-dissociation type.

The ionisation potentials of benzene, biphenyl, and *p*-terphenyl, corresponding to the removal of an electron from the upper π orbitals of these molecules, decrease with the number of phenyl rings in the chain, which is probably associated with the decrease of the energy of the upper filled π orbitals of this series of compounds in consequence of the conjugation between the π electrons of the phenyl groups. This conclusion is confirmed by the fact that the ($\pi\pi^*$) electronic transition band is displaced towards long wavelengths by 2200 cm^{-1} on addition of the phenyl group [32].

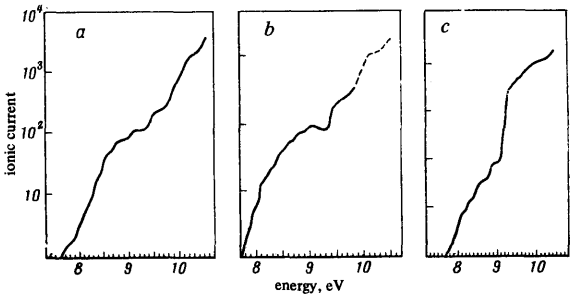


Figure 3. Photoionisation curves: *a*) anthracene; *b*) phenanthrene; *c*) phenothiazine.

A characteristic feature of the electronic structures of the phenyl derivatives of methane (toluene, diphenylmethane, and triphenylmethane) is that the ionisation potentials of these molecules differ little [27]. The insignificant decrease in this series of the energy of removal of electrons from upper filled π orbitals is evidence of only a weak interaction between the π electrons in the phenyl rings in consequence of their non-coplanarity. This feature of the electronic structure is shown also in the decomposition of the phenyl derivatives of methane. For example, the decomposition of triphenylmethane on ionisation takes place with a change in the initial tetrahedral configuration of the molecule and the formation of the stable $(C_6H_5)_3C^+$ ion having a planar configuration.

III. IONISATION POTENTIALS OF AROMATIC COMPOUNDS WITH HETEROATOMS

1. Benzene Derivatives

The substitution of a hydrogen atom in benzene by chromophoric groups may lead to a change in the nature and positions of the upper electronic levels of the ground state of the molecule. The incorporation of the unshared electron pair of the heteroatom in an electron-donating substituent into the π electron system in benzene leads to the removal of the degeneracy of the upper e_{1g} level and the splitting of the energies of the π_3 and π_2 orbitals. The π_3 orbital (b_1 symmetry) corresponds to the maximum electron density at the carbon atom and the π_2 orbital (A_2 symmetry) corresponds to a node. Analysis of the photoelectronic spectra of mono- and *p*-substituted benzene derivatives quoted by Baker et al. [11] shows that the band at 9.40 eV, corresponding to the first vertical ionisation potential of benzene, broadens or splits when the hydrogen atom is substituted (Table 3).

For toluene, diffuse bands corresponding to the first ionisation potential are observed. The splitting of the energies of the π_3 and π_2 levels is probably fairly small

and cannot be determined from the photoelectronic spectrum. The same conclusion follows also from the analysis of the initial section of the photoionisation curve for toluene [5].

Table 3. Vertical ionisation potentials of benzene derivatives according to Turner [11].

Compound	Ionisation potential, eV			$I_{\pi_2}-I_{\pi_3}$	Ionisation potential, eV
	π_3		π_2		π_1
Benzene	—	9.40	—	—	11.5
Toluene	8.9	—	9.13	0.2	—
Phenol	8.75	—	9.45	0.70	—
Anisole	8.54	—	9.37	0.83	11.2
t-Butoxybenzene	8.75	—	9.33	0.58	—
ααα-Trifluoroanisole	—	10.00	—	—	—
ααββδ-Pentafluorophenetole	—	9.97	—	—	—
Chlorophenol	8.69	—	9.75	1.07	—
t-Butoxy-*p*-chlorobenzene	8.72	—	9.76	1.04	—
p-Bromobenzene	8.52	—	9.60	1.08	—
p-Bromoanisole	8.49	—	9.65	1.16	—
p-Dimethoxybenzene	7.90	—	9.19	1.29	—
p-Methoxybenzaldehyde	8.87	—	9.77	0.90	—
Aniline	8.04	—	9.11	1.07	11.5
N-Methylaniline	7.73	—	9.03	1.30	—
NN-Dimethylaniline	7.51	—	9.03	1.52	—
NN-Diethylaniline	7.51	—	9.11	1.60	—
Trifluoro-*N*-dimethylaniline	—	10.00	—	—	—
p-Chloroaniline	8.18	—	9.51	1.33	—
p-Toluidine	7.78	—	9.02	1.24	—
p-*NN*-Dimethyltoluidine	7.48	—	9.06	1.58	—
Fluorobenzene	9.5	—	9.86	—	11.8
Chlorobenzene	9.31	—	9.71	—	12.2
Bromobenzene	9.25	—	9.78	—	11.8
Iodobenzene	8.78	—	9.75	—	—
ααα-Trifluorotoluene	—	9.90	—	—	11.9
Nitrosobenzene	—	9.97	—	—	—
Nitrobenzene	—	10.26	—	—	—
Benzonitrile	—	10.02	—	0.2	11.8
Benzaldehyde	—	9.80	—	—	—
p-Difluorobenzene	9.50	—	10.24	0.74	12.1
p-Chlorofluorobenzene	9.26	—	10.07	0.81	12.3
p-Dichlorobenzene	9.17	—	9.57	0.67	12.7
p-Chloromethylbenzene	8.90	—	9.57	0.67	11.7
p-Chloro-ααα-trifluorotoluene	9.80	—	10.19	0.39	12.5
p-Chloronitrobenzene	9.99	—	10.46	0.45	—
p-Chloronitrosobenzene	9.74	—	10.27	0.53	—
p-Chlorobenzaldehyde	9.59	—	9.88	0.29	12.4
p-Bromochlorobenzene	9.04	—	9.96	0.92	—
p-Dichlorobenzene	8.97	—	9.95	0.98	11.9
p-Bromotoluene	8.71	—	9.45	0.74	—
p-Bromo-ααα-trifluorotoluene	9.55	—	10.02	0.47	—
p-Bromobenzonitrile	9.54	—	10.41	0.87	—
p-Xylene	8.71	—	9.21	0.50	—

In aromatic ethers C_6H_5OR, where the unshared electron pair of oxygen is conjugated with the π electrons of the phenyl group, the π_3 and π_2 orbitals of phenol are split—to the extent of 0.70 and 0.83 eV in the case of anisole. In *p*-butoxybenzene $C_6H_5OC(CH_3)_3$ the splitting is less. It follows from the photoelectronic spectra of alkyl phenyl ethers (Fig. 4 and Table 3) that the second ionisation potential hardly changes but the first decreases on substitution. This finding leads to the conclusion that the substitution of hydrogen by alkyl groups leads to a decrease of the energy of the π_3 orbital with B_1 symmetry, while the energy of the π_2 orbital with A_2 symmetry hardly changes under these conditions. For this reason, the first ionisation potentials of alkyl phenyl ethers (Table 4) correspond to the removal of electrons from the upper π_3 orbitals of type B_1 and decrease in the series phenol, anisole, and phenetole, and the second ionisation potentials correspond to the removal of an electron from the π_2 orbital of type A_2. On passing to benzyl methyl ether, where the conjugation between the unshared pair of the oxygen *p* electrons and the π electrons of the phenyl group is weakened, the first ionisation potential is higher compared with those of alkyl phenyl ethers.

The photoelectronic spectra of trifluoromethyl phenyl ether and pentafluoroethyl phenyl ether do not show a splitting of the first ionisation band due to the breakdown of conjugation between the unshared electron pair of oxygen and the π electrons of the phenyl group. This may be attributed to the powerful inductive effect of the fluorine atoms, which leads to a change in the nature of the unshared electron pair of oxygen and an increase of the energy of the upper π level.

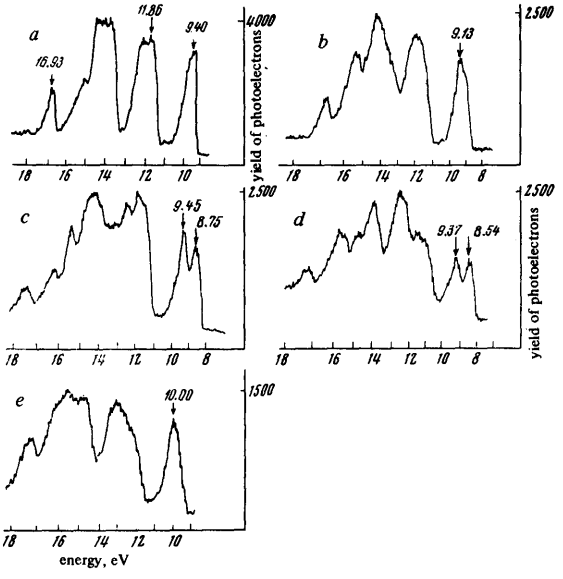


Figure 4. Photoelectronic spectra: *a*) benzene; *b*) toluene; *c*) phenol; *d*) anisole; *e*) $C_6H_5OCF_3$.

Table 4. First adiabatic photoionisation potentials of aromatic compounds containing the $-N\diagdown$, –O–, and –S– groups outside the ring.

Compound	Ionisation potential, eV	Refs.	Compound	Ionisation potential, eV	Refs.
Aniline	7.70±0.02	7	α-Naphthylamine	7.30±0.03	28
N-Methylaniline	7.34±0.03	17	β-Naphthylamine	7.25±0.03	28
NN-Dimethylaniline	7.14±0.03	17	Diphenylamine	7.25±0.03	35
Benzylamine	8.64±0.03	17	Triphenylamine	6.86±0.03	35
m-Toluidine	7.50±0.03	17	Phenol	8.50±0.01	7
NNN'N'-Tetramethylphenylenediamine	6.18±0.05	33	Anisole	8.22±0.02	7
			Phenetole	8.13±0.02	7
			Benzyl methyl ether	8.85±0.03	36
o-Fluoroaniline	7.95±0.02	34			
m-Fluoroaniline	7.90±0.02	34	*o*-Fluorophenol	8.66±0.01	7
p-Fluoroaniline	7.82±0.02	34	Benzenethiol	8.33±0.01	7

The above characteristics of the electronic structures of alkyl phenyl ethers are well illustrated by the position of the upper π-electron levels in the ground state shown in Fig. 5.

For *p*-substituted benzenes containing –OR groups, the splitting of the energies of the π_3 and π_2 orbitals is fairly large (1.0–1.2 eV), but their investigation requires a more detailed examination of the photoelectronic spectra and the photoionisation potentials of the molecules.

The ionisation potentials of aniline and its derivatives in Table 4 were first determined by Viletov and coworkers[17,37,38] and assigned to the removal of electrons from π orbitals. These investigations also showed that in the vicinity of the threshold the photoionisation curves are diffuse and the probability of the formation of molecular ions in the vibrational ground state is low.

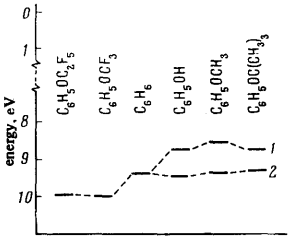


Figure 5. Positions of the upper π-electron levels in the ground state of alkyl phenyl ethers: *1*) π_3 (symmetry B_1); *2*) π_2 (symmetry A_2).

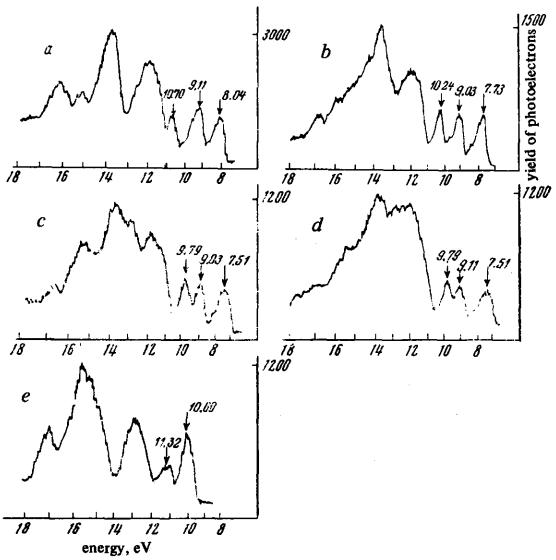


Figure 6. Photoelectronic spectra: *a*) aniline; *o*) *N*-methylaniline; *c*) *NN*-dimethylaniline; *d*) *NN*-diethylaniline; *e*) $C_6H_5N(CF_3)_2$.

The substitution of a hydrogen atom by an amino-group leads to an appreciable separation of the π_3 and π_2 orbitals, mainly due to the decrease of π_3 orbitals of type B_2 which correspond to maximum electron density at the point of substitution. For aniline, this splitting is 1.07 eV and, on consecutive substitution of hydrogen atoms in the amino-group by CH_3 groups, amounts to 1.3 eV for *N*-methylaniline and 1.52 eV for *NN*-dimethylaniline (Table 3 and Fig. 6).

The second ionisation potentials of aniline and its derivatives, associated with the removal of electrons from π_2 orbitals of type A_2 with an electron density node at the point of substitution, remain virtually constant.

The substitution of hydrogen atoms in the alkyl groups by fluorine atoms [$C_6H_5N(CF_3)_2$] leads to the breakdown of conjugation between the unshared electron pair of nitrogen and the π electrons of the phenyl group and the displacement of the first ionisation band towards higher energies. The absence of conjugation between the unshared electron pair of nitrogen and the π electrons of the phenyl group in benzylamine also leads to an increase of the first ionisation potential compared with aniline and its derivatives. It is interesting to note that decomposition processes with abstraction of a hydrogen atom from the methylene group, associated with ionisation as a result of the removal of an electron from the orbital of the unshared pair in the amino-group, are observed for benzylamine at a photon energy exceeding 9.5 eV.[37]

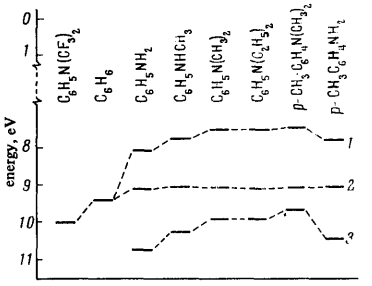


Figure 7. Positions of the upper π-electron levels of aniline and its derivatives: *1*) π_3 (B_1 symmetry); *2*) π_2 (A_2 symmetry); *3*) $\pi 2p_Z$ (–N<).

The photoelectronic spectrum of aniline in Fig. 6 also shows that the third ionisation potential (vertical) of 10.70 eV corresponds to the removal of an electron from the π orbitals with maximum electron density at the nitrogen atom. The third adiabatic ionisation potential of aniline determined from the photoionisation curve is 10.2 eV.[37] It is interesting to compare the change in the third vertical ionisation potential of aniline, as hydrogen atoms in the amino-group are substituted, with the first ionisation potentials of aliphatic amines:

NH_3	CH_3NH_2	$(CH_3)_2NH$	$C_6H_5NH_2$	$C_6H_5NHCH_3$	$C_6H_5N(CH_3)_2$
10.16 eV	9.18 eV	8.36 eV	10.70 eV	10.24 eV	9.79 eV

Fig. 7 shows the positions of the upper filled electronic levels of aniline and its derivatives showing that the separation between the π_3 and π_2 orbitals decreases as the hydrogen atoms in the amino-group are substituted by alkyl groups, owing to the decrease of the energy of the π_3 orbital with B_1 symmetry. Under these conditions, the energy of the π_2 orbital with A_2 symmetry remains virtually unchanged for all aniline derivatives. The nature of the change in the energy of the $\pi(2p_Z)$ orbital associated with the unshared $2p_Z$ electron pair of nitrogen is the same as for the π_3 orbital.

Analysis of the photoelectronic spectra of $C_6H_5CF_3$, C_5H_5CN, C_6H_5NO, and $C_6H_5NO_2$ shows that the first ionisation band is not split but is displaced towards higher energies (the ionisation potentials of these molecules exceed that of benzene). This may be attributed to the transfer

of charge from the benzene ring to the substituents owing to the inductive effect (CF_3) and the negative mesomeric effect (–CN, $-NO_2$).

The ionisation potentials of mono- and *p*-substituted benzenes corresponding to the removal of an electron from the lower π_1 orbital, analogous to the $\pi_1(a_{2u})$ orbital of benzene, as a rule exceed the second ionisation potential of benzene (11.49 eV).[11] This is shown more clearly by halogeno-derivatives of benzene and the rule of addivity holds most satisfactorily when substituents are introduced into the 1- and 4-positions (Table 3).

The change in ionisation potentials associated with the removal of an electron from the σ_{CC} orbitals can also be followed in halogeno-derivatives of benzene. Thus the ionisation potential corresponding to the removal of an electron from the σ_{CC} orbital changes on substitution of hydrogen by fluorine from 16.83 to 17.4 eV and on substitution by chlorine and bromine the changes are to 16.7 and 17.0 eV respectively.

The above analysis of the electronic structure of benzene derivatives based on the photoionisation potentials is confirmed also by theoretical calculations. The calculation by the Pariser–Parr–Pople method showed[39] that in aniline the non-bonding electrons of nitrogen are conjugated with the π-electrons of the phenyl ring. The upper filled $3b_1$ and $1a_2$ aniline π orbitals have electronic configurations similar to those of the corresponding upper $2b_1$ and $1a_2$ benzene π orbitals and the lower $1b_1$ aniline π orbital corresponds to the lower $1b_1$ benzene π orbital. The $2b_1$ aniline π orbital, which is located between the $1a_2$ and $1b_1$ orbitals, has the maximum electron density at the nitrogen atom.

The substitution of hydrogen atoms in the amino-group of aniline by phenyl groups leads to a lowering of the first ionisation potential to 7.25 eV (diphenylamine) and 6.68 eV (triphenylamine)[35]. This finding may be attributed to a decrease of the energies of the upper π orbitals in consequence of the conjugation between the phenyl rings via the unshared pair of nitrogen. Calculations by the LCAO-MO method showed that compounds such as diphenylamine have a single π-electron system[40]. The conjugation between the unshared pair of nitrogen and the π-electron system of the aromatic group in α-naphthylamine and β-naphthylamine also leads to a decrease of the energies of the upper π orbitals and hence the ionisation potentials.

2. Nitrogen-containing Heterocyclic Compounds

The ionisation potentials of azines were investigated in studies on photoionisation[7,41] and photoelectronic spectroscopy[9,15,42,43] (Tables 5 and 6).

Information about the nature and energies of the π and n orbitals from which electrons are abstracted on ionisation may be obtained by comparing the experimental ionisation potentials with the calculations of the wave functions and the energies of azabenzenes and azanaphthalenes[42,44,45].

It has been shown[42] that the energies of the upper π orbitals in the ground states of benzene, pyridine, and pyrazine are the same, while those for pyrimidine and pyridazine are higher by 0.4 eV. The energy of the n orbital of the unshared pair of nitrogen does not change in the series pyridine, pyrazine, and pyrimidine, but decreases for pyridazine in consequence of the powerful Coulombic interaction between the electrons of the two unshared pairs of nitrogen. On this basis, the first adiabatic ionisation potentials of pyridine and pyrazine, 9.31 and 9.36 eV respectively (Table 5), were assigned to the removal of an electron from the π orbital and the first ionisation potentials of pyrimidine and pyridazine were attributed to the removal of an electron from the n orbital of the unshared pair of nitrogen.

Table 5. First adiabatic ionisation potentials of nitrogen-containing heterocyclic compounds.

Compound	Ionisation potential, eV	Refs.	Compound	Ionisation potential, eV	Refs.
Benzene	9.246±0.005	9	Phthalazine	8.68	42*
Pyridine	9.32±0.03	7	Anthracene	7.41	18
Pyrazine	9.29±0.01	41	Acridine	7.78±0.03	28
Pyrimidine	9.35±0.01	41	Phenazine	8.4	23
Pyridazine	8.90	42*	2-Methylpyridine	9.02±0.03	7
Naphthalene	8.14±0.02	43	3-Methylpyridine	9 04±0.03	7
Quinoline	8.62±0.01	41	4-Methylpyridine	9.04±0.03	7
Isoquinoline	8.55±0.02	41	2,3-Dimethylpyridine	8.85±0.02	7
Quinoxaline	9.02±0.01	41	2,4-Dimethylpyridine	8.85±0.02	7
Quinazoline	9.02	42*	2,6-Dimethylpyridine	8.85±0.02	7
Cinnoline	8.51	42*			

* The ionisation potentials were determined by photoelectronic spectroscopy.

Table 6. First and upper ionisation potentials of heterocyclic compounds[42].

Compound	Ionisation potential, eV							
Pyridine	9.31	(9.51)	10.45	12.30	—	13.83	—	—
Pyrazine	9.36	(9.51)	10.15	11.14	11.73	13.13	(13.38)	14.78
							16.0	16.60
Pyrimidine	9.42	(9.64)	10.39	11.06	13.62	(13.82)	15.56	16.75
Pyridazine	8.90	(9.22)	10.53	11.16	13.63	(13.83)	15.70	16.64
Quinoline	8.62	9.07	10.64	11.42	13.07	(13.65)	15.05	16.20
Isoquinoline	8.54	9.24	10.50	11.60	(12.54)	(13.26)	15.98	16.69
Quinoxaline	8.99	10.72	11.58	(12.32)	(13.98)	15.30	16.21	17.07
Quinazoline	9.05	9.74	10.72	11.26	12.02	(13.78)	16.28	17.23
Cinnoline	8.51	9.03	9.75	10.83	12.04	12.46	13.85	16.16
Phthalazine	8.68	9.17	9.68	10.77	12.07	(12.58)	14.09	15.23
Pyrrole (Ref.10)	8.22	—	9.03	12.38	14.23	17.08	—	—
Furan (Ref.10)	8.77	—	10.21	12.62	—	—	—	—

Calculation of the energies of the filled orbitals of pyridine, pyrazine, and pyrimidine by the more accurate SCF MO method[42] confirmed the assignment of the first ionisation potentials of the azabenzenes and also showed that the energies of the n orbitals of nitrogen in pyridine and pyrazine slightly exceed (by 0.01–0.1 eV) the energies of the upper π orbitals. This permits the assignment of the second ionisation potentials of pyridine and pyrazine, each of which is 9.51 eV, to the removal of an electron from the orbital of the unshared pair of nitrogen. Analysis of the ionisation potentials of azabenzenes also permits an interpretation of the upper ionisation potentials of pyridine on the basis of the calculation of the orbital energies by the SCF MO method. Thus the ionisation threshold at 10.45 eV may be attributed to the removal of an electron from the $2b_1$ π orbital or the upper σ orbital. Such assignment of the ionisation potentials of pyridine was not made in earlier studies on photoelectronic spectroscopy[10] and Rydberg absorption spectra[16], because the second ionisation potential at 9.51 eV had not been observed.

Information about the nature of the π and n orbitals in the ground state of pyridine and pyrazine was obtained by calculating all the wave functions for the molecules by the SCF MO method[44,45], based on the derivation of special Gauss functions.

It was shown that the upper $1a_2$ pyridine π orbital has a node at the nitrogen atom and an equal charge distribution at the carbon atoms. This property of the upper $1a_2$ π orbital is clearly reflected in the similarity of the first adiabatic ionisation potentials of pyridine and benzene and also in the fact that the substitution of hydrogen atoms by methyl groups in pyridine in different positions leads to a decrease of the first ionisation potential by virtually the same amount. For example, the ionisation potentials of methylpyridines are in the range 9.02–9.04 eV. Finally, it should be noted that there is a linear relation between the first ionisation potentials of pyridine derivatives and those of the corresponding benzene derivatives[10]. This correlation constitutes yet another proof that the first ionisation potential of pyridine corresponds to the removal of an electron from the upper π orbital with A_2 symmetry. The substitution of hydrogen atoms by alkyl groups leads to a decrease of the π-orbital energies owing to the inductive effect.

Data have also been obtained[44,45] on the nature of the orbitals of the unshared pairs of the nitrogen atoms in pyridine and pyrazine. The $11a_1$ orbital of the unshared pair of the nitrogen atom in pyridine is partially delocalised (to the extent of 0.6 charge units) over the carbon and hydrogen atoms. The unshared pairs of the nitrogen atoms in pyrazine are non-equivalent both in type and as regards energy. The upper $11a$ pyrazine n orbital is delocalised, as in pyridine, while the lower $10a_1$ orbital is only slightly delocalised. The determination of the relative energy of this orbital requires a further detailed examination of the photoelectronic spectrum and the photoionisation curve of pyrazine.

The interpretation of the ionisation potentials of azanaphthalenes was achieved on the basis of the first-order perturbation theory by an empirical selection of corrections to the orbital energies derived from the first ionisation potentials of naphthalene, quinoline, and isoquinoline, obtained from the photoelectronic structures of these compounds[42]. It was shown that the first ionisation potentials of quinoline, isoquinoline, quinoxaline, and quinazine correspond to the removal of an electron from the upper π orbital and the first ionisation potentials of phthalazine and cinnoline correspond to the removal of an electron from the upper n orbital of the unshared pair of the nitrogen atom. This conclusion is consistent with data on the photoionisation of quinoline, isoquinoline, quinoxaline, phthalazine, and cinnoline[41].

Gencha and El-Sayed[41] observed on the photoionisation curves of pyrazine and pyridine a vibrational level structure in the vicinity of the first ionisation potential and attributed it to the planar vibrations of the molecular ion (by analogy with the corresponding vibrations of these molecules in the ground state)[46,47]. However, these data require revision, since the first and second ionisation potentials of azabenzenes corresponding to the removal of an electron from the π and n orbitals are similar.

The ionisation potentials of acridine and phenazine, associated with the removal of an electron from the π and n orbitals, were obtained from the electronic absorption spectra of their complexes with iodine and chloranil[23,24,48]. Acridine and phenazine are n donors in relation to iodine and π donors in relation to chloranil. The ionisation potentials calculated from the absorption spectra and corresponding to the removal of an electron from the upper filled π orbital are 7.9 and 8.4 eV respectively.

It is interesting to note that the ionisation potentials of pyridine, quinoline, and acridine on the one hand and the energies of the π,π^* and n,π^* triplet levels are correlated. For example the energy of the excited n,π^* triplet level of pyridine exceeds by 0.3 eV the energy of the lower π,π^* triplet level[49,50] and the second ionisation potential of pyridine, corresponding to the removal of an electron from the n orbital of nitrogen, exceeds by 0.2 eV the first ionisation potential corresponding to the removal of an electron from the upper $1a_2$ π orbital. However, there is no such correlation between the ionisation potentials and the excitation energies of the singlet levels of azines of this type, because the energy of the n,π^* level is even lower than the energy of the π,π^* level. This discrepancy between the ionisation and excitation energies is due to the fact that the energy of the π,π^* level exceeds that of the n,π^* level by only 0.45 eV, while the singlet–triplet splitting of the π,π^* level of pyridine is 1.1 eV, exceeding the singlet–triplet splitting of the n,π^* level by 0.75 eV.

3. Compounds with a Carbonyl Group

The first ionisation potentials of aromatic compounds containing a carbonyl group were determined in a number of studies[7,12,28,51] (Table 7).

Table 7. First photoionisation potentials of aromatic compounds containing the groups $\diagdown$N–, –O–, –S–, and $\diagdown$C=O.

Compound	Ionisation potential, eV	Refs.	Compound	Ionisation potential, eV	Refs.
p-Benzoquinone	9.95	12	Pyrrole	8.20±0.01	7,56
9,10-Anthraquinone	9.34±0.03	28		8.22	10**
	9.55	51***	*N*-Methylpyrrole	8.09±0.01	56
Fluorenone	9.42	51***	*N*-n-Butylpyrrole	7.87±0.02	56
Benzaldehyde	9.55±0.03	28	2-Methylpyrrole	7.78±0.1	56
	9.53±0.03	7	3-Methylpyrrole	7.90±0.02	56
Acetophenone	9.27±0.03	7	2,4-Dimethylpyrrole	7.54±0.02	56
Acridone	7.60±0.03	6	Furan	8.89±0.01	7
N-Methylacridone	7.53±0.03	6	2-Methylfuran	8.39±0.01	7
N-Ethylacridone	7.49±0.03	6	Furfural	9.21±0.01	7
N-Phenylacridone	7.46±0.03	6	Thiophen	8.86±0.01	7
Phenothiazine	7.7	21	2-Chlorothiophen	8.86±0.01	7
	7.62	18*	2-Bromothiophen	8.63±0.01	7
9,10-Dihydroacridine	7.24±0.03	6			

* Spectroscopy.
** Photoelectronic spectroscopy.
*** Electron impact.

It has been shown[51] that the first ionisation potential of 9,10-anthraquinone (9.55 eV) corresponds to the removal of an electron from the orbital of the unshared pair of oxygen and the second ionisation potential (10.24 eV) corresponds to the removal of an electron from the π orbital. The energy of the singlet π,π^* level of anthraquinone is higher than the energy of the n,π^* level by an amount close to the difference between the second and first ionisation potentials. There is a similar correlation also between the ionisation potentials of 9,10-anthraquinone and the energies of the triplet n,π^* and π,π^* levels[52]. This assignment of the ionisation potentials is consistent with the calculation for the 9,10-anthraquinone molecules by the Pariser–Parr–Pople method[53]. It has also been shown[53] that the first ionisation potentials of *p*-benzoquinone (9.95 eV) and benzaldehyde (9.55 eV) corresponds to the removal of an electron from the orbital of the unshared

electron pair of the oxygen atom in the carbonyl group. This interpretation of the ionisation potentials agrees with the positions of the lower electronic singlet and triplet levels of *p*-benzoquinone and benzaldehyde[54].

4. Heterocyclic Compounds containing the Groups >N–, –O, and –S–

The unshared electron pair of the heteroatom (nitrogen, oxygen, and sulphur) in compounds of this type may be incorporated in the π-electron system of the molecule, and leads to a change of the nature of the π orbitals in the ground state and an appreciable splitting of the upper π levels of the molecules.

The question of the nature and relative positions of the electronic levels of pyrrole, furan, and thiophen remained unresolved for a long time until the studies on photoionisation and photoelectronic spectroscopy[10].

The first ionisation potentials of pyrrole, furan, and thiophen (Table 7) were determined by the photoionisation method and attributed to the removal of electrons from the π orbitals[7]. The upper ionisation potentials of pyrrole and furan have also been investigated by Turner[10] (Table 6).

The interaction of the unshared electron pair of the nitrogen atom with π electrons in the pyrrole molecule is fairly pronounced, which leads to the removal of the degeneracy of the π_3 and π_2 orbitals and the separation of their energies by 0.8 eV (Table 2). On this basis, one may assume that the π-electron system of pyrrole consists of three filled $1a_2$, $2b_1$, and $1b_1$ π orbitals. The first and second ionisation potentials of pyrrole (8.22 and 9.03 eV) correspond to the removal of electrons from the $1a_2$ and $2b_1$ orbitals.

Information on the nature of the π orbitals of pyrrole from which electrons are removed on ionisation and about the distribution of electron density at the carbon, hydrogen, and nitrogen atoms was obtained from the calculation of all the wave functions of pyrrole by the SCF MO method[55]:

Distribution of π electron density in pyrrole.

Atom in five-membered ring	$1a_2\pi$ orbital	$2b_1\pi$ orbital	$1b_1\pi$ orbital
N ($2p_z$)	—	0.76	0.9
C_2 ($2p_z$) ± C_5 ($2p_z$)	1.40	0.03	0.72
C_3 ($2p_z$) ± C_4 ($2p_z$)	0.60	1.21	0.38

The upper $1a_2$ π orbital, the energy of which corresponds to the first ionisation potential, has an electron density node at the nitrogen atom and a maximum at the adjacent carbon atoms (1.40). The second, $1b_1$ π orbital has an electron density node between the nitrogen atom and the centre of the molecule, a maximum at the carbon atoms not linked to the nitrogen atom, and a minimum at the nitrogen atom. The lower $1b_1$ π orbital of pyrrole embraces the entire molecular skeleton and has an electron density maximum at the nitrogen atom. Analysis of the wave functions also shows that the nitrogen atom in pyrrole "loses" 0.34 charge units to the π orbital and "acquires" 0.75 charge units from the σ orbital. Trigonal hybridisation in pyrrole is appreciably modified for nitrogen ($s^{1.37}p^{2.38}$) but for carbon remains virtually unchanged ($s^{1.06}p^{2.10}$).

It is interesting to compare data on the distribution of electron density in pyrrole with the changes in the first ionisation potential corresponding to the removal of an electron from the $1a_2$ orbital on substitution of a hydrogen atom by a methyl group in various positions, determined by the present author and Yuzhakova[56]. Table 7 shows that the maximum decrease of the first ionisation potential (by 0.42 eV compared with the first ionisation potential of pyrrole) is observed for 2-methylpyrrole, i.e. on substitution of the hydrogen atom by a methyl group at the carbon atom adjoining the nitrogen atom; at this carbon atom the $1a_2$ π orbital has a maximum electron density. The minimum change of the first ionisation potential is observed on substitution of the hydrogen atom by a methyl group at the nitrogen atom, where the $1a_2$ π orbital has an electron density node (*N*-methylpyrrole). Naturally, the replacement of a hydrogen atom by an n-butyl group does not lead to an appreciable decrease of the first ionisation potential (*N*-n-butylpyrrole).

In furan the separation of the energies of the π_3 and π_2 orbitals is even greater than in pyrrole (1.44 eV) (Table 6). The energy of the unshared pair of oxygen, which does not participate in the conjugation with the π electron system, exceeds the energies of the upper π orbitals[10].

Earlier it was noted that a characteristic feature of the electronic structure of anthraquinone is that the upper level of the ground state is populated by the unshared electron pair of the oxygen atom in the carbonyl group[51]. However, the nature and relative positions of the n and π electronic levels in the ground state change significantly on introduction of an amino-group into the conjugated system, which happens in acridone and its derivatives. The electronic spectra of acridone and its derivatives show that the first long-wavelength absorption band in their spectra corresponds to the ($\pi\pi^*$) electron transition and that the unshared electron pair of the amino-group participates in the exchange interaction with the electrons in the π orbitals[57].

The first ionisation potentials of acridone, *N*-methylacridone, *N*-ethylacridone, and *N*-phenylacridone (Table 7) are in the range of energies 7.6–7.46 eV and correspond to the energies of the removal of electrons from the upper π orbitals. Indeed the exchange interaction of the unshared electron pair of nitrogen with the π electrons of the molecule leads to an appreciable (compared with anthraquinone) rise of the upper π level of acridone and its derivatives, i.e. a decrease of the ionisation potential. It is necessary to remember that the energy of the non-bonding orbital of the oxygen atom in the carbonyl group changes little when the dimensions and the nature of the π-electron system are altered.

The insignificant change in the first ionisation potentials in this series is evidence that the position of the upper π level alters little under these conditions. The fact that the ionisation potential of *N*-phenylacridone is close to those of [other] acridone derivatives suggests in turn that the phenyl group is located outside the plane of the molecule.

The removal of an electron from the upper π orbital of 9,10-dihydroacridine, where there is no carbonyl group, requires a somewhat lower energy (0.2–0.3 eV) compared with *N*-alkyl derivatives of acridone. The closeness of the ionisation potentials of 9,10-dihydroacridine and diphenylamine[35] is evidence that the π-electron systems of these molecules are isoelectronic.

Phenothiazine, the first ionisation potential of which is also associated with the removal of an electron from the upper π orbital[11], should be included in this type of heterocyclic

compounds, where the heteroatom supplies two non-bonding electrons to the π-electron system. A characteristic feature of the photoionisation curve of phenothiazine at higher energies is a steep rise in the region of 9.15 eV, corresponding to the second ionisation potential of the molecule.

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Thus the above analysis of the ionisation potentials of aromatic compounds permits definite conclusions concerning the nature and positions of the electronic levels of the molecules from which electrons are removed on ionisation.

The electronic structure of aromatic compounds containing heteroatoms outside the ring, the unshared electron pair of which is incorporated in the π-electron system (aniline and its derivatives, alkyl phenyl ethers), is characterised by the presence of four π orbitals. The energies of the upper π_3 and π_2 orbitals of compounds of this type are separated (compared with benzene), mainly due to the decrease of the energy of the π_3 orbital with B_1 symmetry (Figs. 6 and 7). The mass spectra of these compounds reveal their relative stability on ionisation. However, in those cases where the conjugation between the unshared electron pair of the heteroatom and the π electrons of the phenyl group is weak (for example in benzylamine), the stability of the molecules decreases owing to their decomposition into ions and radicals.

A characteristic of the structure of heterocyclic compounds, the π-electron system of which includes an unshared electron pair (pyrrole, furan) is that the upper electronic level in the ground state of molecules of this type corresponds to the π orbital with A_2 symmetry, which has an electron density node at the heteroatom. This type of upper π orbitals is clearly revealed by the different first ionisation potentials of pyrrole and its derivatives.

The ionisation potentials of nitrogen-containing heterocyclic compounds (azines), in which each heteroatom supplies one p-electron to the π-electron system, correspond to the removal of an electron from the upper π orbitals. Pyrimidine, pyridazine, phthalazine, and cinnoline, the first ionisation potentials of which correspond to the removal of an electron from the orbitals of the unshared electron pair of the nitrogen atom, are an exception.

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