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Photoelectron He^{I} spectra of fluorinated azo- and azoxy-benzenes

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Abstract

The electronic structure of azobenzene, $C_6H_5N{=}NC_6H_5$, azoxybenzene, $C_6H_5N(O){=}NC_6H_5$, and their fluorinated derivatives, including some fluorinated azobenzenes with substituents in the *para* position ($X = CH_3$, OCH_3, CF_3, CN, NO_2, Br), have been studied by photoelectron spectroscopy. Spectral interpretation has been carried out using quantum-chemical MNDO calculations and literature data regarding the electronic structure of related compounds. In the spectra of the azobenzenes, a group of bands lying in the range of low ionization energies corresponds to four π-orbitals of the benzene rings and one σ-orbital localized on the N=N bond. For azoxybenzenes, a similar group of bands refers to four π-MOs and one orbital of an oxygen electron lone pair. The contribution of fluorine orbitals to the upper occupied π-MOs is small and the changed energy of these orbitals may be explained mainly by the inductive effect.

Introduction

The interaction of substituents with the aromatic π-system essentially determines the reactivity of aromatic compounds. This interaction is characterized by the inductive and resonance terms which adequately represent the main influence of the substituent effect on the reactivity of the benzene ring. An understanding of the physical sense of such a division should stimulate an investigation of the details of molecular electronic structure. An essential tool in such studies is photoelectron spectroscopy which allows the determination of the energies of the ground and electronically excited states of the ion. The spectra may be analyzed using quantum-chemical calculations associated with the results for related compounds [1–5]. In the one-electron approximation, the analysis involves comparing the ionization energy measured with the calculated molecular orbital energy of opposite sign, and thus determinating the correlation between the ionization energies and electron density distribution of the given MO.

The introduction of fluorine into the benzene ring is known to cause the so-called 'perfluoro effect', i.e. a predominant stabilization of the σ-orbitals relative to the π-orbitals [6, 7]. This results in more clear-cut bands

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TABLE 1

Ionization energies of azobenzene and its fluorinated derivatives

Compound	Ionization energies (eV)											
I	8.4 4$a_u\pi$	8.75 $a_g\sigma_N$		9.3 3$a_u\pi$+3$b_g\pi$			9.8 2$b_g\pi$					
II	8.5 $a_u\pi$	8.8 $a_g\sigma_N$		9.6 $a_u\pi+b_g\pi$			9.9 $b_g\pi$			11.7 π		
III	8.7 π	9.1 σ_N		9.85 π		10.2 $\pi+\pi$						
IV	9.2 $a_u\pi$		9.8 $\sigma_N+a_u\pi+b_g\pi$			10.5 $b_g\pi$		12.1			12.3	
V	9.27 π		9.92 $\sigma_N+\pi+\pi$		10.45 π		12.2 π			13.95		
VI	9.4 $a_u\pi$		10.0 $a_u\pi+b_g\pi+a_g\sigma_N$			10.6 $b_g\pi$	12.3 π			12.8 π		
VII	8.75 $a_u\pi$		9.45 $\sigma_N+a_u\pi+b_g\pi$			10.0 $b_g\pi$	11.2			12.1		
VIII	9.4 $a_u\pi+a_u\pi+b_g\pi+\sigma_N$					10.15 $b_g\pi$		11.8			12.1	
IX	10.0 $a_u\pi+a_u\pi+b_g\pi$				10.6 σ_N	11.1 $b_g\pi$		12.7			13.0	
X	10.2 $a_u\pi+a_u\pi+b_g\pi+\sigma_N$					11.0 $b_g\pi$	12.2			12.7		
XI	10.25 $a_u\pi+a_u\pi+b_g\pi+a_g\sigma_N$					11.0 $b_g\pi$		12.0			13.3	
XII	9.2 $a_u\pi$		9.75 $a_u\pi+b_g\pi$		10.15 σ_N	10.8 $b_g\pi$	11.25 n_{Br}		11.55 n_{Br}		12.1	12.6

for aromatic π-orbitals and the substituent π-orbitals in C_6F_5X compared to C_6H_5X, since the highest occupied MOs of the σ and π type have different energies. Moreover, it has been shown earlier [8] that the fluorine 2p atomic orbitals (AOs) make little contribution to the highest occupied molecular orbital (HOMO) of fluorinated benzenes, although in accumulation they could affect the HOMO energies.

It seemed reasonable to consider the interaction of substituents containing multiple bonds and two aryl fragments with the aromatic π-system. For electron-accepting substituents, no essential splitting of the phenyl b_1 and a_2 MOs was observed in view of the deeper location of the valence levels. This has been shown, for example, for nitrobenzene [9] and pentafluoronitrobenzene [10] where the NO_2 group only interacts weakly with the highest occupied MOs of the phenyl and pentafluorophenyl groups and there is practically no contribution of the 2p AOs of heteroatoms to the HOMO. Substituent–ring interaction takes place mainly in the system of internal valence σ- and π-orbitals. In contrast, in aniline [11] and pentafluoroaniline [12] molecules, there is considerable splitting of the upper π-MOs, suggesting π-interaction between the NH_2 substituent and the benzene ring.

The aim of the present work was the measurement and interpretation of the photoelectron spectra of compounds of the type Ar–N=N–Ar and Ar–N(O)=N–Ar in order to derive information about the intramolecular π-interaction between the aryl ring and the bridge fragments –N=N– and –N(O)=N–.

Results and discussion

Table 1 lists the ionization energies of azobenzene $C_6H_5N{=}NC_6H_5$ (**I**) and its derivatives with the substituents 4,4′-F (**II**), 2,2′,4,4′-F (**III**), 2,2′,3,3′,5,5′,6,6′-F (**IV**), 2,2′,3,3′,4,4′,5,5′-F (**V**), and of decafluoroazobenzene $C_6F_5N{=}NC_6F_5$ (**VI**) and its derivatives with the substituents 4,4′-OCH_3 (**VII**), 4,4′-CH_3 (**VIII**), 4,4′-CF_3 (**IX**), 4,4′-CN (**X**), 4,4′-NO_2 (**XI**) and 4,4′-Br (**XII**).

Figures 1 and 2 depict their spectra. The energy values for the band maxima measured by ourselves in the spectra of **I** and their assignment from MNDO calculation results are in good agreement with the literature data [13, 14] taken as the basis for the interpretation of the photoelectron spectra of fluorinated azobenzenes. The order of the highest occupied orbitals of azobenzene is $4a_u$, $a_g(\sigma_N)$, $3a_u$, $3b_g$, $2b_g$ in the C_{2h} symmetry group (the gas-phase molecules were suggested as having the *trans* conformation).

Judging by the results of MNDO calculations, the four upper π-orbitals mainly consist of bonding and antibonding combinations of the $2b_1$ and $1a_2$ MOs of the benzene rings (Fig. 3). The contribution of the nitrogen 2p AOs is 5–10% for the $4a_u$ and $2b_g$ orbitals and zero for $3a_u$ and $3b_g$ MOs consisting of the a_2 MOs of the benzene rings. These orbitals have similar energies

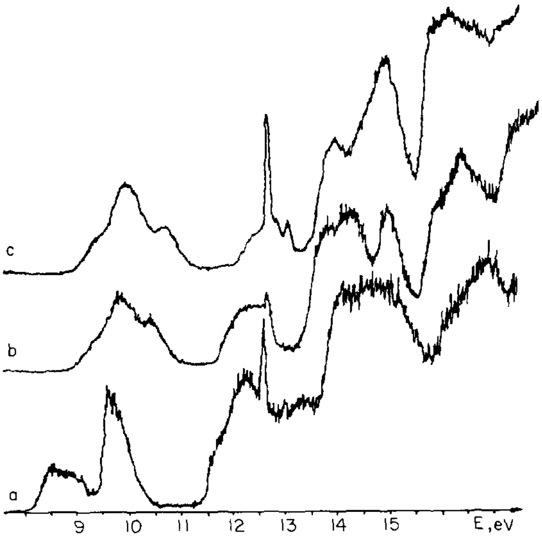


Fig. 1. Photoelectron spectra of fluorinated azobenzenes (a, compound **II**; b, compound **IV**; c, compound **VI**).

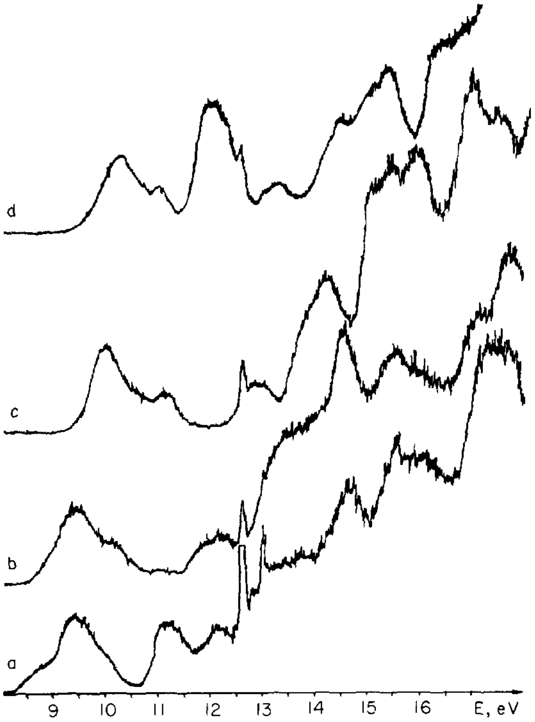


Fig. 2. Photoelectron spectra of fluorinated azobenzenes with substituents in the *para* positions (a, compound **VII**; b, compound **VIII**; c, compound **IX**; d, compound **XI**).

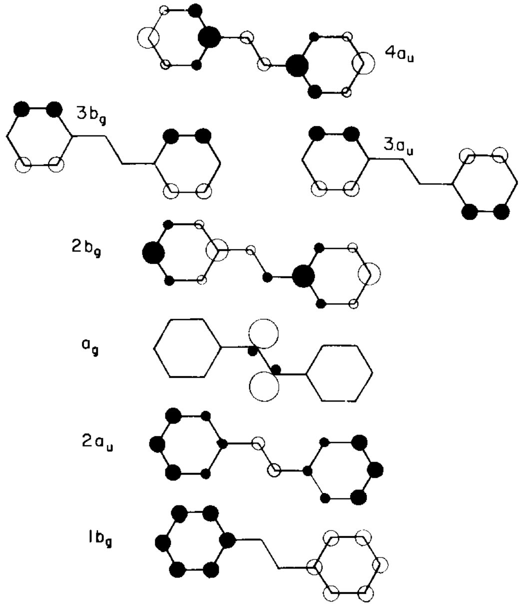


Fig. 3. The highest occupied molecular orbitals of azobenzene.

and correspond to a group of overlapping bands in the ionization energy range 9 eV in the spectrum.

If the value of the azo group–benzene ring interaction is expanded into its components, the inductive effect of the group will be about zero while the conjugation effect, when estimated as the benzene MO b_1 destabilization, will be 0.85 eV (in the spectrum of benzene the first band has a maximum energy of 9.24 eV, and in the spectrum of azobenzene the first band has a maximum energy of 8.4 eV). As far as the antibonding combination of electron lone pairs of the nitrogen atoms $a_g(\sigma_N)$ is concerned, the corresponding calculation somewhat underestimated its energy in comparison to the highest π-MOs, but even so it was still essentially higher than for the rest of the σ- and π-type orbitals.

In the spectrum of azomethane $CH_3N{=}NCH_3$, the band corresponding to the $a_g(\sigma_N)$ orbital has a maximum energy of 8.98 eV [15, 16]. Since the methyl and phenyl fragments possess similar inductive effects, no essential shift in this band should be expected for azobenzene ($\Delta E = 0.13$ eV). The low-lying π-MOs $2a_u$, $1b_g$ and $1a_u$ represent combinations of the nitrogen 2p AOs and the $1b_1$ orbitals of the benzene rings. The greatest contribution of the nitrogen 2p AOs should be expected for the lowest lying π-orbital $1a_u$ (up to 70%), whose band possibly lies in the 14 eV ionization energy range. The bonding combination of the electron lone pairs of nitrogen $b_u(\sigma_N)$ is strongly delocalized and does not differ in this respect from other σ-orbitals incorporating the nitrogen 2p AOs.

Electronic structure calculations for some fluorinated azobenzenes show that substitution of hydrogen by fluorine should lead to a systematic shift of the band to the range of larger ionization energies. Such a band shift corresponding to the π-MOs may be described qualitatively in terms of the inductive and conjugation effects. The inductive effect is proportional to the number of fluorine atoms and depends only slightly on the substitutional position, while the magnitude of the conjugation effect is proportional to the square of the value of the one-electron wavefunction in the substitution position and will be different, for example, for isomeric molecules. Hence, fluorination of azobenzene at the *para* position should lead to inductive stabilization of the $3a_u$ and $3b_g$ orbitals for the group at the substitution position, whereas the $4a_u$ and $2b_g$ MOs also experience the conjugation effect through a diminution in their total stabilization.

The spectrum of compound **II** differs from that of compound **I** in that the four first bands are shifted to the large ionization energy range. The band shift corresponding to the $3a_u$ and $3b_g$ MOs is 0.3 eV, that of the bands of the $4a_u$ and $2b_g$ MOs is 0.1 eV, whilst that of the band of the $a_g(\sigma_N)$ orbital is 0.05 eV. The adiabatic ionization energy value of the group of bands in the 12 eV region increases by 0.2 eV, while a band with an energy of 11.7 eV appears in the spectrum. If we follow the order of orbitals suggested by Millefiori and Millefiori [13, 14], this band should be assigned to the bonding combination of the electron lone pairs of the nitrogens, $b_u(\sigma_N)$. However, fluorination generally leads to stronger stabilization of the σ-orbitals which accommodate the AO contributions of aromatic carbons and hydrogens than of π-type orbitals. Taking into consideration calculation data on the essential delocalization of the $b_u(\sigma_N)$ orbital and the value of the fluorination effect for σ- and π-type orbitals, one should assign the band with the maximum energy at 11.7 eV to the π-orbital of a_u symmetry [the analogue of the $2a_u$ orbital in compound **I**].

Further support for such an assignment may be obtained from a comparison of the spectrum of compound **I** with that of fluorobenzene. On substitution of hydrogen by an azoxy group, the shift of the first band is 0.85, and the same or smaller shift should be expected for the $2b_1$ MO band of fluorobenzene. In the spectrum of compound **II**, the band for the corresponding orbital must have an energy of about 11.4 eV, which is close to the true value of 11.7 eV.

In molecule **III** only the symmetry plane is preserved (the C_s group), but the highest five orbitals bear some similarity to those of molecule **II** since the contribution of the fluorine p AO to them is small. The effect of fluorine is seen more clearly when we compare the electronic structure of molecules **I** and **IV**. The $4a_u$ and $2b_g$ orbitals are very much stabilized by the inductive effect of fluorine, the energy difference between them remaining virtually unchanged. The $3a_u$ and $3b_g$ orbitals are stabilized to a lesser extent, which is again due to the conjugation effect of the fluorine 2p AO with the aromatic π-system.

In the spectrum of 1,2,4,5-tetrafluorobenzene, the a_2 and b_1 MO bands have energies of 9.5 and 10.2 eV. Substitution of hydrogen by the azo group leads to an insignificant (approximately 0.3 eV) shift in the a_2 MO bands to the high-energy range and an opposite shift of 1 eV occurs with the b_1 MO band. Similar shift values are observed on hydrogen substitution by the azo group in benzene and monofluorobenzene molecules, i.e. in compounds **I** and **II**. With the $2a_u$ and $1b_g$ orbitals, the fluorine effect is incapable of expansion into the conjugation and inductive effects because of the absence of a substitution position with a zero wavefunction. The main contribution to these MOs is made by the π-orbitals of the benzene rings of b_1 symmetry. The fluorine 2p AOs form a system of orbitals in the 16 eV energy range where their contribution to the MOs is approximately 70%.

The spectra of the isomeric molecules **IV** and **V** differ only slightly from each other, the band shift being less than 0.1 eV which on taking account of their essential width is within experimental accuracy.

The ionization energies corresponding to the σ- and π-MOs increase with the extent of fluorination: in the spectrum of compound **VI**, the energy of the first vertical transition is increased by 1 eV relative to that for azobenzene (**I**). However, on moving from benzene to pentafluorobenzene, the first band is shifted to the higher energy range by the extent of 9.24–9.9 eV. Such a discrepancy may be explained by the smaller conjugation between the fluorine 2p AO and the aromatic b_1 MO due to the appreciable contribution of the nitrogen p-orbitals to the highest MO. Judging by the calculation results, the order of the four highest π-MOs and of the a_g σ-orbital remains the same.

In most cases, the complex contour may not be separated into bands; hence for compounds **IV**–**VI** listed in Table 1 the positions of the band maxima are recorded rather than the separate values of the ionization energies. Indeed, for compound **VI** there is some problem in assigning the band at 12–13 eV which may involve one or two orbitals of the σ or π type. As demonstrated by numerous experimental data, however, the σ-MOs should be strongly stabilized and for this reason the band most probably refers to π-type orbitals. Judging by relative intensity, this band is more likely to correspond to two orbitals rather than one. According to the calculation results, two orbitals a_u and b_g similar to the orbitals $2a_u$ and $2b_g$ of azobenzene lie in the energy range 12–13 eV, and the splitting value must not exceed 0.5 eV. Such splitting corresponds to the band width of 1 eV in the spectrum.

For fluorinated azobenzene with the substituents CH_3O, CH_3, CF_3, CN, NO_2 or Br introduced into the *para* position, the character of intramolecular interactions between the π-system and fragments possessing the π-orbital may be conveniently described in terms of the conjugation and inductive effect. As shown by calculation, the π-orbitals of substituents make the greatest contribution to the low-lying MOs, their contribution to the four highest π-orbitals being small.

In the spectrum of compound **VII**, the band with an energy maximum at 11.2 eV corresponds to the orbital localized on the oxygen atoms. In contrast to the spectrum of the non-fluorinated analogue, where the band has the energy maximum of 10.4 eV, fluorination of benzene rings leads to a shift in this band to the higher energy region of 0.8 eV [14]. Approximately the same shift is observed for the bands of the five highest occupied MOs, which may be interpreted as indicating roughly the same contribution from the fluorine orbitals to these MOs.

The substitution of hydrogen in molecule **IV** by a CH_3 group leads only to a slight (0.1–0.2 eV) band shift to the higher energy range. However, fluorination of the methyl groups in compound **VIII** increases the inductive effect on the highest orbitals and leads to a band shift to higher energies. The CF_3 group is conjugated to the benzene ring to a slightly smaller extent than the methyl group, since the band of the b_g orbital is shifted from 10.15 eV to 11.1 eV, while the bands of the $a_u + b_g$ orbitals which have zero electron density in the substitution position are shifted from 9.4 eV to 10.2 eV. A still greater difference in the value of the conjugation effect is observed for the CF_3 group and the fluorine atom: the shift of the first band may be estimated to be 0.6 eV, while the shift of the $a_u + b_g$ orbitals is virtually zero.

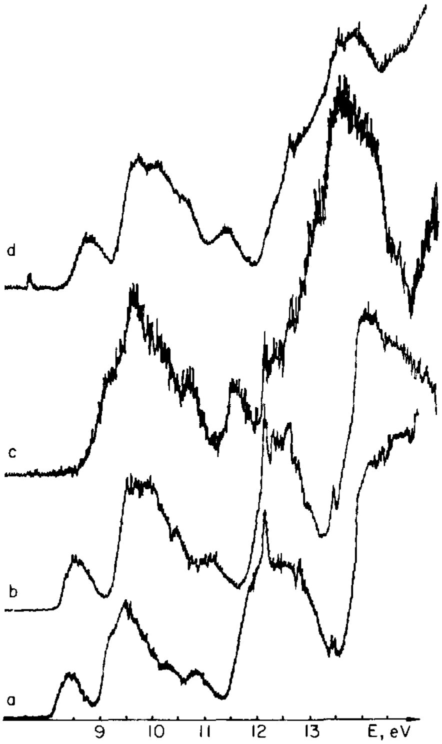
The spectrum of compound **X**, with the CN groups in the *para* position being between 9.5 eV and 12.0 eV, is almost the same as that of compound **IX**, indicating a comparable electrostatic effect value for CN and CF_3 groups. In the spectrum of pentafluorobenzonitrile, C_6F_5CN, the band corresponding to the π-MO of b_1 and a_2 symmetry has a maximum energy at 10.45 eV, implying that the –N=N– fragment is a poorer electron acceptor than the fluorine atom.

The first band group in the spectrum of compound **XI** is almost the same in form as the total contour for the spectra of the preceding compounds. This band is only shifted to the higher energy range by approximately 0.1 eV relative to the spectrum of compound **X**, where the substituent is the CN group. The energy range 11.5–12.5 eV includes a band for a group of orbitals localized on the NO_2 group, and similar bands are observed in the spectrum of tetrafluoronitrobenzene (the maximum energy in this case is approximately 12 eV).

Bromination of fluorinated azobenzene at the *para* position leads to bands with energies of 11.25 eV and 11.55 eV, corresponding to orbitals localized on the substituent atoms. In the spectrum of compound C_6F_5Br, the corresponding band has a maximum energy of 11.5 eV. The assignment of the first bands in the spectrum of compound **XII** given in Table 1 has been made by analogy with the remaining compounds.

The inductive effect of a substituent on the molecular orbital energies should correlate with the value of the inductive σ-constant: electron-accepting groups will stabilize the $a_g(\sigma_N)$, $3a_u$ and $3b_g$ orbitals, while electron-donating groups will destabilize them. For the orbitals $4a_u$ and $2b_g$ which have non-zero electron density in the *para* position, the similar tendency must be complicated by the conjugation effect. The band shift of orbitals similar to the $3a_u$ and $3b_g$ orbitals of azobenzene in that series of compounds constructed to illustrate the variation in the inductive properties of the substituents (CH_3, H, OCH_3, CN, NO_2, Br, CF_3, F) should increase in accord with some tendency. However, the experimental values (9.4, 9.8, 9.45, 10.2, 10.25, 9.75, 10.0, 10.0) show no such tendency, which may be explained either by inaccuracies in the determination of the ionization energies or by the absence of a purely inductive effect due to the broken symmetry of the molecules.

Table 2 lists the ionization energies of azoxybenzene $C_6H_5N(O){=}NC_6H_5$ (**XIII**) and of its derivatives with the substituents 4,4'-F (**XIV**), 2,2',6,6'-F (**XV**), 2,2',4,4'-F (**XVI**), 2,2',3,3',5,5',6,6'-F (**XVII**), and of decafluoroazoxybenzene $C_6F_5N(O){=}NC_6F_5$ (**XVIII**) and 4,4'-CF_3-octafluoroazoxybenzene (**XIX**). Their spectra are shown in Figs. 4 and 5. The results of electronic structure calculations show that the π-systems of the α and β benzene rings in the azoxybenzene molecule, i.e. (α)–ArN=N(O)Ar–(β), interact weakly; hence, the orbitals can be conveniently designated as approximately independent fragments. In interpreting the spectrum of azoxybenzene (**XIII**), we start from data previously listed [11, 12, 14] and the results of our studies on the electronic structure of fluorinated azobenzenes.



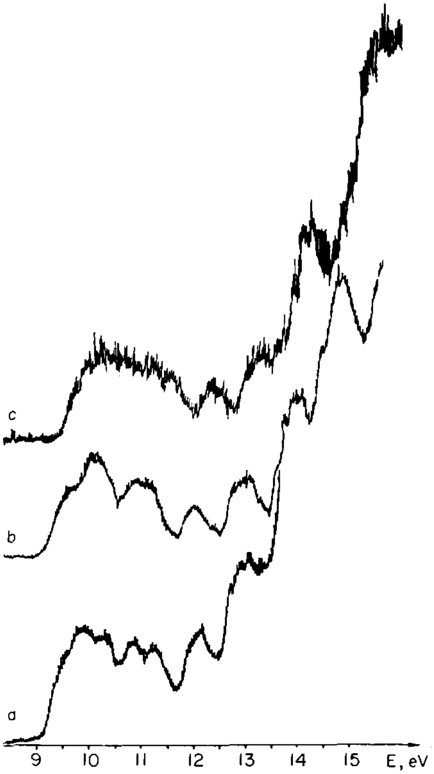


Fig. 4. Photoelectron spectra of fluorinated azoxybenzenes (a, compound **XIII**; b, compound **XIV**; c, compound **XV**; d, compound **XVI**).

Fig. 5. Photoelectron spectra of fluorinated azoxybenzenes (a, compound **XVII**; b, compound **XVIII**; c, compound **XIX**).

TABLE 2

Ionization energies of azoxybenzene and its fluorinated derivatives

Compound	Ionization energies (eV)								
XIII	8.35		9.16		9.46	9.59	9.87	10.28	10.86
	$b_1(\alpha)$		$a_2(\alpha)$		σ_O	$a_2(\beta)$	$b_1(\beta)$	π_{NNO}	σ_N
XIV	8.51		9.51		9.95		10.44	11.4	
	$b_1(\alpha)$		$a_2(\alpha)+\sigma_O$		$b_1(\beta)+a_2(\beta)$		π_{NNO}	σ_N	
XV	9.18		9.6		10.1		10.65	11.52	12.4
	$b_1(\alpha)$		$a_2(\alpha)+a_2(\beta)+\sigma_O$		$b_1(\beta)$		π_{NNO}	σ_N	$b_1(\beta)$
XVI	8.8		9.62		9.64	10.06	10.14	10.69	11.37
	$b_1(\alpha)$		$a_2(\alpha)$		σ_O	$b_1(\beta)$	$a_2(\beta)$	π_{NNO}	σ_N
XVII	9.34	9.66		9.91	10.29	10.76	11.24	12.0	12.7
	$b_1(\alpha)$	$a_2(\alpha)$		σ_O	$a_2(\beta)$	$b_1(\beta)$	π_{NNO}	σ_N	
XVIII	9.53	9.91		10.13	10.39	10.84	11.23	12.0	12.78
	$b_1(\alpha)$	$a_2(\alpha)$		σ_O	$a_2(\beta)$	$b_1(\beta)$	π_{NNO}	σ_N	
XIX	9.75		10.2		11.15	11.6	12.3	13.2	
	$b_1(\alpha)$		$a_2(\alpha)+\sigma_O$		$a_2(\beta)+b_1(\beta)$	π_{NNO}	σ_N		

Comparison of the electronic structures of compounds **I** and **XIII** shows that addition of an oxygen atom to the nitrogen bridge does not lead to any essential change in the energies of the highest π_1 and π_4 MOs which makes a significant contribution to the b_1 orbitals of the benzene rings. However, the bands of π_2- and π_3-MOs which originally have the same maximum energy are separated by 0.5 eV in the spectrum of compound **XIII**. These orbitals consist of aromatic a_2 MOs and are not conjugated with the π-system of the NNO fragment. The splitting may be attributed to the different values of the inductive effect for the α and β benzene rings due to the non-equivalence of the nitrogen atoms. According to the calculation results, the charges on the NNO atoms are equal to -0.19, 0.37 and -0.43, respectively. Thus, the inductive and conjugation effect values for the α benzene ring are approximately 0.1 and 0.8 eV, and for the β ring 0.2 and 0.35 eV.

The σ-MO of the nitrogen lone–pair electrons of a_g symmetry disappears in going from azo- to azoxy-benzene and is replaced by the σ-MO of the electron lone pair of oxygen. In the ionization energy range 8–11.5 eV, one would expect bands corresponding to the π-MO localized on the NNO fragment and the σ-MO of the electron lone pair of two-coordinated nitrogen. Taking into account the calculation results and assuming the azoxybenzene molecule to be planar, one can identify five bands corresponding to seven orbitals in the ionization energy range 8–11.5 eV: five π-type MOs and two σ-orbitals for the oxygen and nitrogen electron lone pairs (Fig. 6). Thus the order of the orbitals in the azoxybenzene molecule is as follows: $b_1(\alpha)$, $a_2(\alpha)$, σ_O, $a_2(\beta)$, $b_1(\beta)$, π_{NNO}, σ_N.

Another factor used in assigning the second band is its form, i.e. a steep front and small width at half-height. The electron density distribution of this orbital in azo- and azoxy-benzene should have a similar symmetry, and the character of the bonding should not essentially change on removal of the electron. Such an assumption is consistent with the result observed: the second band in the spectrum of azoxybenzene and the third band in the spectrum of azobenzene have a steep front and small width at half-height.

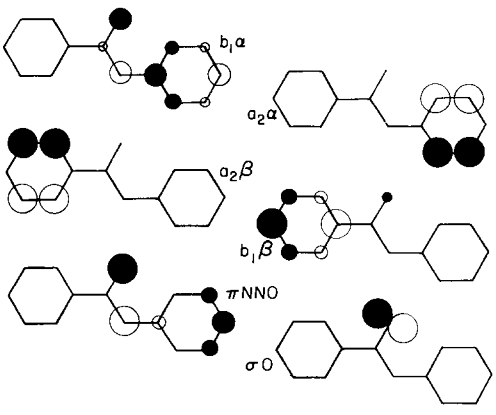


Fig. 6. The highest occupied molecular orbitals of azoxybenzene.

It should be noted that in the molecule of *N*-benzylideneaniline, $C_6H_5CH{=}NC_6H_5$, a non-planar geometry is possible with the benzene ring bent around the C(Ar)–N bond at an angle of 35° [17]. Attempted estimation of the angle of bending of the benzene ring relative to the NNO plane using the least difference in the π-MO energies and the experimentally observed ionization energies for compound **XIII** gave a value of 0°, i.e. the planar conformation.

On substitution of hydrogen by fluorine atoms, all the π-MOs experience a stabilizing inductive effect, while the orbitals having a maximum electron density in the substitution position are destabilized by the conjugation effect. The greatest stabilization on substitution of hydrogen by fluorine in the 4,4′-positions of compound **XIII** should be experienced by the $a_2(\alpha)$ and $a_2(\beta)$ orbitals and the smallest stabilization by the $b_1(\alpha)$ and $b_1(\beta)$ orbitals. The calculated energies of the $b_1(\beta)$ and $a_2(\beta)$ MOs differ by 0.08 eV. Such a coincidence must show itself as a double intensity band in the spectrum of compound **XIV**. This assumption agrees with the experimental result: double intensity bands are observed in the spectrum and correspond to the $a_2(\alpha)+\sigma_O$ orbitals (maximum energy 9.51 eV) and $b_1(\beta)+a_2(\beta)$ MOs (energy 9.95 eV).

In estimating the effect of hydrogen substitution by fluorine in positions 2,2′,6,6′ of molecule **XIII**, it is necessary to take the molecular geometry into account. Optimization has shown that the α ring in molecule **XV** should be orthogonal to the NNO plane, and that the relative independence of the π-orbitals of the aryl fragments must be preserved. The highest occupied MO should be the $a_2(\alpha)$ orbital having an electron density maximum at the 2 and 6 positions. The angle between the α benzene ring and the NNO plane is probably less than 90° in fact, and the order of orbitals differs from the calculated one: judging by its width and shift in comparison to the spectrum of **XIII**, the first band should be assigned to the $b_1(\alpha)$ orbital as in the spectra of the other azoxybenzenes. The band with an energy maximum at 10.1 eV corresponds to the $b_1(\beta)$ MO which is more stabilized than the $a_2(\alpha)$ and $a_2(\beta)$ MOs.

Molecule **XVI** could have a planar geometry if the fluorine atoms at 2,2′ are in the *trans* position relative to oxygen. In this case, the highest occupied orbital is $b_1(\alpha)$ with an insignificant contribution from the fluorine 2p AO. In the spectrum of compound **XVI**, the first band separated by 0.85 eV from the group of overlapping bands, indicates a planar geometry for the molecule and the efficiency of π-interaction between the b_1 MO of the benzene ring and the NNO orbitals.

The spectra of compounds **XVII–XIX** are similar to the spectrum of **XV** in that the first band has a shoulder form arising from a large array of overlapped bands, the ionization energy value increasing constantly with the degree of fluorination. The first band in the spectra of these compounds should be assigned to the $b_1(\alpha)$ orbital with an insignificant contribution arising from the p AO of fluorine.

If one looks at the shifts of bands corresponding to the π_{NNO} and σ_N orbitals, it is seen that the ionization energies vary in a non-monotonic manner when plotted against the number of fluorine atoms, although the conjugation effect can have little effect on the orbitals localized on the NNO fragment. This non-monotonic variation may be explained by the changed molecular geometry which arises on substitution of hydrogen by fluorine; in particular, the torsion angles of the benzene rings relative to the NNO plane may vary from 0° to 90°.

The fluorination effect in the spectra of compounds **XVII–XIX** leads to the disappearance of the bands associated with the σ-MO of the benzene rings, i.e. the bands of the fluorinated rings lying in the high-energy range. The double intensity band whose maximum has an energy of 12.9–13.2 eV may be assigned to the π-orbitals, one of which is the bonding combination of the b_1 MOs of the benzene rings and the antibonding MO of the N–O bond, whilst the other is the antibonding combination of the same orbitals $b_1(\alpha)$–$b_1(\beta)$ with a small contribution from the p AO of oxygen.

The fluorine p AOs make a considerable contribution to both of these low-lying orbitals. On sequential substitution of hydrogen atoms in compound **XVII** by fluorine atoms and CF_3 groups, the first band is shifted systematically to the high ionization energy range, the shift for the CF_3 group being greater than for the fluorine atom.

Experimental

The compounds used in this study were similar to those previously described [18–20]; their purities were determined by GLC methods, ^1H and ^{19}F NMR spectroscopy and elemental analysis. Photoelectron He^I spectra were recorded on a spectrometer designed at Leningrad State University [21], which was built and located at the University in Vladivostok. The spectra were calibrated using the Xe lines (IP_1, 12.13; IP_2, 13.43 eV). The accuracy of the IP values was ± 0.02 eV (or for the broad bands, ± 0.08 eV) at 60–150 °C. The photoelectron He^I spectra have also been measured on an ES-3201 spectrometer. In view of the observed energy scale drift of this instrument during the course of an experiment, the multiscan mode was used with subsequent correction of each scan by summation [22]. The maximum energies of the overlapped bands and their width were estimated by expansion into Gaussian terms using a set of spectrum-processing programs. The quantum-chemical calculations of the electronic structures were performed using the MNDO method with model geometry [23, 24]. Bond lengths (Å): N=N, 1.24; N–O, 1.228; N–C, 1.43; C–C, 1.4; C–H, 1.1; C–F, 1.33; $\angle$N=N–C, 113°. For the molecules **XV** and **XVI**, the torsion angle α of the benzene rings relative to the NNO plane as determined by geometry optimization was 90°; the remaining molecules were taken to be planar.

Conclusions

It has been found that the highest π-orbitals of the benzene rings in the azobenzene molecules interact with the π-MO of the bridge –N=N–. The greatest contribution to this π-interaction is made by the low-lying orbital of a_u symmetry. Fluorination of the benzene rings and introduction of electron-accepting substituents into the *para* positions leads to a rearrangement of the highest π-levels which may be explained by the conjugation effect and by their inductive stabilization. Addition of oxygen to the nitrogen bridge makes the benzene rings non-equivalent and changes both the localization and energy of the highest π-orbitals. The highest occupied π-orbital of azoxybenzene is localized on the benzene ring bonded to the two-coordinate nitrogen atom. The value of the interaction between the highest π-MOs of the benzene rings with the NNO fragment is comparable to that in the azobenzene molecule. The greatest contribution to the π-bonding is made by the low-lying orbital consisting of the $1b_1$ MOs of the benzene rings and the bonding orbital of the NNO fragment. Fluorination of benzene rings, as in the azobenzene molecule, does not lead to any essential rearrangement of the π-system.

References

1 D. W. Turner, C. Baker, A. D. Baker and C. R. Brundle, *Molecular Photoelectron Spectroscopy*, Wiley-Interscience, London, 1970, 386pp.
2 J. H. D. Eland, *Photoelectron Spectroscopy*, Butterworth, London, 1974, 321pp.
3 J. W. Rabalais, *Principles of Ultraviolet Photoelectron Spectroscopy*, Wiley-Interscience, New York, 1977, 454pp.
4 V. I. Nefedov and V. I. Vovna, *Electronay structura organicheskich i elementoorganicheskich soedinenii*, Moscow, Nauka, 1988, 199pp.
5 C. R. Brundle and A. D. Baker (eds.), *Electron Spectroscopy, Theory, Techniques and Application*, Academic Press, London, Vol. 1, 1977, 460pp.; Vol. 2, 1978, 288pp.; Vol. 3, 1979, 362pp.
6 C. R. Brundle, M. B. Rubin, N. A. Kuebler and H. J. Basch, *J. Am. Chem. Soc.*, *94* (1972) 1451.
7 G. G. Furin, A. V. Zibarev, L. N. Mazalov and V. D. Yumatov, *Electronay structura ftororganicheskich soedinenii*, Nauka, Novosibirsk, 1988, 264pp.
8 G. G. Furin, G. G. Yakobson, V. D. Yumatov, L. N. Mazalov and A. V. Okotrub, *J. Fluorine Chem.*, *28* (1985) 241.
9 V. D. Yumatov, V. V. Murachtanov, N. F. Salakhutdinov, A. V. Okotrub, L. N. Mazalov, L. N. Logunova, V. A. Koptyug and G. G. Furin, *Zh. Struct. Khim.*, *28* (1987) 73.
10 A. V. Okotrub, V. D. Yumatov, L. N. Mazalov, G. G. Furin, V. V. Murachtamov and L. G. Bulysheva, *Zh. Struct. Khim.*, *29* (1988) 76.
11 M. H. Palmer, W. Moyes, M. Spiers and J. N. A. Ridyard, *J. Mol. Struct.*, *53* (1979) 235.
12 G. G. Furin, A. Sh. Sultanov and I. I. Furley, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1987) 580.
13 S. Millefiori and A. Millefiori, *J. Chem. Soc., Faraday Trans. 2*, *77* (1981) 245.
14 S. Millefiori and A. Millefiori, *Can. J. Chem.*, *59* (1981) 821.
15 D. C. Frost, S. T. Lee, C. A. McDowell and N. P. C. Westwood, *J. Chem. Phys.*, *64* (1976) 4719.
16 S. Millefiori, E. Ciliberto, A. Millefiori and M. A. Zerbo, *Spectrochim. Acta*, *37A* (1981) 605.
17 L. Klasinc, B. Ruscic, G. Heinrich and H. Gusten, *Z. Naturforsch., Teil B*, *32* (1977) 1291.
18 I. K. Korobeinicheva, O. M. Fugaeva and G. G. Furin, *J. Fluorine Chem.*, *39* (1988) 373.
19 Yu. G. Shermolovich, O. M. Polumbrik, L. N. Markovsky, E. P. Saenko, G. G. Furin and G. G. Yakobson, *Zh. Org. Khim.*, *13* (1977) 2589.

20 O. I. Andreevskay, S. A. Krupoder, L. N. Markovsky, G. G. Furin, Yu. G. Shermolovich and G. G. Yakobson, *Zh. Org. Khim.*, *16* (1980) 822.

21 N. E. Petrachenko, M. E. Akopyan, V. I. Kleymenov, M. V. Kleymenov, I. V. Korkoshko, M. M. Timoshenko and Yu. V. Chizhov, *Vestn. LGU*, *4* (1983) 29.

22 D. V. Yudin, N. E. Petrachenko and V. I. Vovna, *Stroenie veshestva i svoistvo molekul*, Izdat. Dalnevostochnogo universiteta, Meshvuz. sborn. Vladivostok, 1987, p. 160.

23 D. V. Yudin and V. V. Gorchakov, *Zh. Prikl. Khim.*, *49* (1988) 642.

24 M. J. S. Dewar and W. J. Thiel, *J. Am. Chem. Soc.*, *99* (1977) 4899; *ibid.*, *99* (1977) 4907.