STRUCTURE OF MATTER
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Photoelectron Spectra and Electron Structure of Boron Difluoride Ethyl Acetonate, Boron Difluoride Benzoyl Acetonate, and Its Derivatives

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Abstract—The electron structure of boron fluoride acetyl acetonate $F_2B(OCCH_3)_2CH$, boron fluoride benzoylacetonate, and two its derivatives is investigated by ultraviolet electron spectroscopy and quantum chemistry in an approximation of the all-electron density functional theory. Sequences and preferential localization of the π levels of conjugated cycles are established, and the violation of coplanarity of the cycles in the presence of the methyl group in the *ortho* site of the substituent is shown. It is concluded that the values of the ionization energy and the calculated data indicate a sequential increase in the contribution of π orbitals of the benzoic cycle in the UOMO (upper occupied molecular orbital) upon substituting CH_3 groups for hydrogen atoms.

Keywords: electron structure, boron difluoride β-diketonates, photoelectron spectroscopy, all-electron density functional theory.

INTRODUCTION

Complex compounds of boron difluoride with β-diketonate ligands containing aromatic cycles at the carbonyl carbon atoms possess intense luminescence, which leads to their use as laser dyes, organic light emitting diodes, and in materials for electrophotography and nonlinear optics [1, 2]. The synthesis of new luminescent compounds assumes knowledge of the interrelations of optical properties with the electron structure of already obtained phosphors. The most widespread and trustworthy information on the valence levels of these complexes can be acquired by ultraviolet photoelectron spectroscopy (UPS) of the vapors in combination with quantum−chemical simulation [3−5].

We published the results of our investigations for some complexes of boron difluoride in [4, 6, 7]. However, the theoretical calculations in semiempirical approximations did not allow us to unambiguously interpret the photoelectron spectra even in the region of ionization energies (IE) of n_0 and π orbitals. The all-electron density functional theory (DFT), which allows for electron correlation, allowed us to revise our interpretation of the UPS and to obtain geometry and electron parameters of complexes that agreed better with our experiments.

In this work, we present the results from theoretical and UPS investigations of F_2BAA (I) and three

β-diketonate complexes of boron fluoride containing the benzene cycles
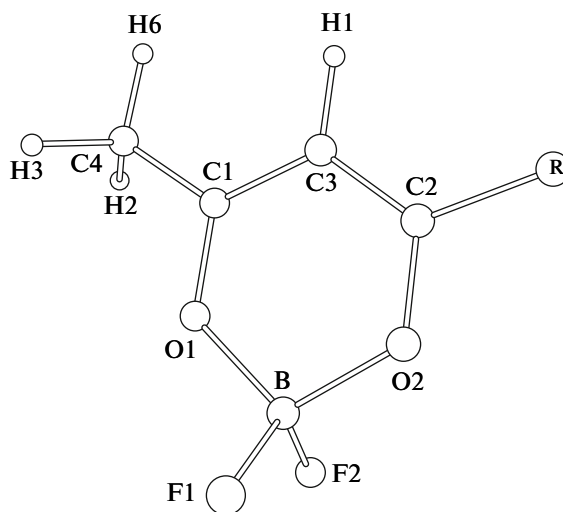
I: R = CH_3 (F_2BAA is boron difluoride acetylacetonate)

II: R = C_6H_5 (F_2BBA is boron difluoride benzoylacetonate)

III: R = 4-$CH_3C_6H_4$ (F_2BTA is boron difluoride toluylacetonate)

IV: R = 2,4-$(CH_3)_2C_6H_3$ (F_2BXA is boron difluoride xyloylacetonate)

To determine more precisely the effect of the AOs of the two fluorine atoms on the distribution of the electron density of ligand MOs of the π type and n

Table 1. Geometry parameters and orders of bonds for F_2BAA, F_2BAA^+, and LiAA

Bond	F_2BAA		F_2BAA^+		LiAA		Angle	F_2BAA	F_2BAA^+	LiAA
	R_{AB}, Å	P_{AB}	R_{AB}, Å	P_{AB}	R_{AB}, Å	P_{AB}		value of angle, deg		
B−F1	1.39	1.00	1.35	1.06	−	−	F1−B−F2	115	122	−
B−O1	1.53	0.64	1.59	0.49	1.77	0.33	O1−B−O2	107	103	105
O1−C1	1.32	1.22	1.28	1.42	1.30	1.40	B−O1−C1	125	129	121
C1−C3	1.40	1.33	1.46	1.04	1.41	1.29	O1−C1−C3	121	119	124
C1−C4	1.49	0.92	1.48	0.94	1.51	0.89	C1−C3−C2	120	121	125

orbitals of oxygen, we also calculated the structure and discuss the results for the simplest acetylacetonate of metal, LiAA.

EXPERIMENTAL

The photoelectron spectra were obtained using an ES-3201 electron spectrometer with a HeI radiation source ($h\nu = 21.2$ eV). The temperature of the ionization cuvette was varied from 20 to 200°C, depending on the sublimation temperature of complexes. The spectrometer resolution under the experimental conditions was no lower than 0.08 eV; xenon was used to calibrate the scale of the electron energy. The accuracy in determining the location of the band peaks was not lower than 0.02 eV. The spectra were interpreted based on the regularities in the PE spectra of the compounds under study and related compounds in combination with the calculated results.

To compare the vertical IEs with the orbital energies, we used an extended variant of Koopmans' theorem:

$$IE_i = -\varepsilon_i + \delta_A,$$

where δ_A is the correction to the orbital energy (Koopmans' defect), which depends on the employed functional, the character of the MO, and the density of the electron states in the valence band.

Calculations were performed by DFT using the FIREFLY quantum−chemical program [8]. We used the B3LYP5 hybrid exchange-correlation functional. For all of the atoms, we selected the 6-311G basis, which is relatively economical from the viewpoint of computational time and satisfactorily describes the electron structure of β-diketonates containing aromatic cycles. The initial geometry was taken from [1]. Calculation of the Hessian performed for all the molecules confirmed the correspondence of the optimized structures to the points of the local minimum on the surface of the potential energy.

RESULTS AND DISCUSSION

The interatomic distances, orders of the bonds, and the angles between the bonds for F_2BAA are presented in Table 1, along with similar data for the ionized com-

plex and LiAA. Interatomic distances $R_{A−B}$ and orders of the bonds $P_{A−B}$ for the complex of p-element boron differ noticeably from the corresponding values in the complex of s-element lithium not only with respect to the M−O bonds, but also to the bonds of the organic fragment of the cycle.

Optimizing the geometry parameters of the F_2BAA complex led to the configuration with the lowest energy corresponding to a screened location of three hydrogen atoms: two hydrogen atoms of methyl groups and a hydrogen atom at the γ carbon atom of the chelate cycle. A similar arrangement of hydrogen atoms was also characteristic of three other II−IV complexes. For compounds II and III, violation of the coplanarity of two cycles did not exceed 1°, while for compound IV, the steric factors expanded the dihedral angle between the planes to 25°. The violation in C_{2v} symmetry caused by substituting the aromatic cycle in F_2BAA for one methyl group led to minor differences (0.01−0.02 Å) in the lengths of the B−O and C−C bonds.

The photoelectron spectrum of F_2BAA (Fig. 1) differs from the known spectra of the acetylacetonates of metaelements $M(AA)_n$ ($n = 1, 2, 3$) [3, 9], first by anomalously high values of the IE of ligand levels, and second by the overlap of four to five bands in the region of 12.5−13.5 eV, masking the band of n_+ electrons. To demonstrate the effect of the two fluorine atoms on the distribution of the electron density and the MO energy of the chelate cycle, the forms of some upper filled orbitals for F_2BAA and LiAA are presented in Fig. 2, and the energies of the Kohn−Sham orbitals, experimental IEs, and the contribution from atoms and methyl groups are given for two complexes in Table 2.

Substitution F_2B for the lithium atom in the acetylacetonate complex leads to stabilization of two upper levels by 1.94 and 2.38 eV, according to the calculated data, while the values of vertical IEs increase by 1.60 and 2.24 eV, respectively (Table 2). Such considerable stabilization is due mainly to a reduction in the overall electron density at the ligand atoms, from −0.64e in LiAA to −0.12e (in our approximation of the analysis of the electron density according to Mulliken). The boron atom has a positive charge of +0.86e, exceeding the charge of the lithium atom, but boron transfers the
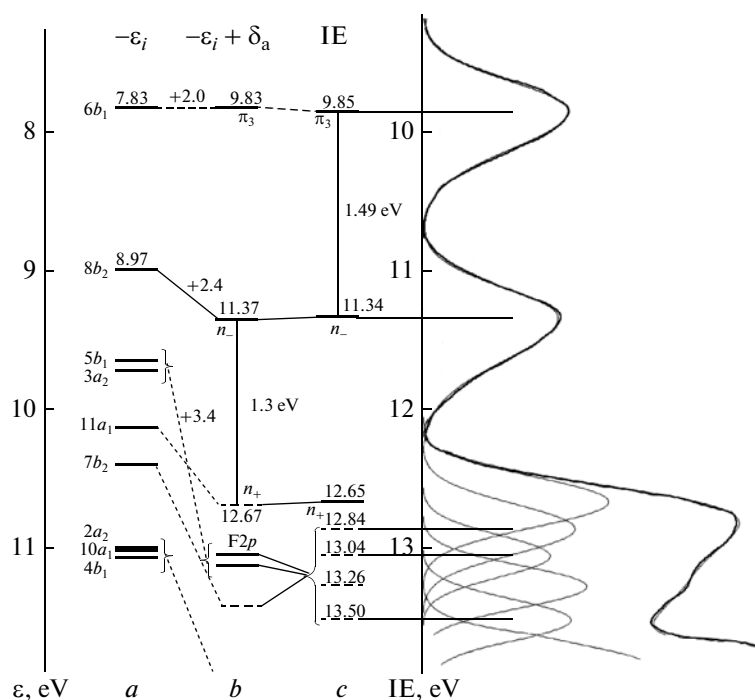
Fig. 1. Photoelectron spectrum and energy diagrams for F_2BAA: (*a*) energy of the Kohn–Sham orbitals; (*b*) MO energies corrected by δ (2.0 eV for π_3, 2.4 eV for n, and 3.4 eV for $F2p$); and (*c*) experimental IEs, including the results from expansion of the third band.
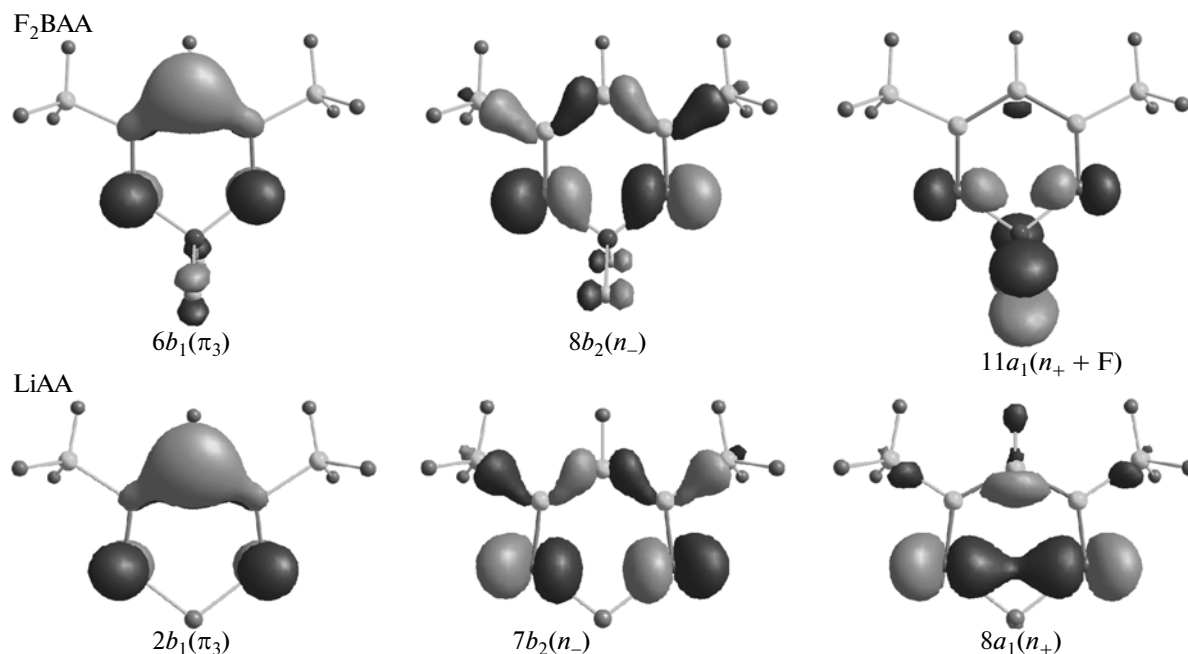

Fig. 2. Forms of MO for metal cycles LiAA and F_2BAA.

electron density to the two fluorine atoms (0.74 eV) rather than to the ligand atoms.

The two upper MOs in both complexes make similar contributions to the ligand atoms and bonding characters. For LiAA, the third $8a_1(n_+)$ and fourth

$2a_2(\pi_2)$ orbitals are localized preferentially on the oxygen atoms. According to the calculated data, however, there are two levels below the $8b_2(n_-)$ MO that are localized preferentially on the fluorine atoms (Table 2), while the n_+ orbital contributes to the fully symmetric

Table 2. Orbital energies (ε_i), vertical IE, and compositions of MOs for acetylacetonate complexes of lithium and boron difluoride (where q is the effective charge)

MO	$-\varepsilon_i$, eV	Contributions from atoms and groups, %					IE, eV
		B	2O	3C	2F	2CH$_3$	
LiAA							
$2b_1(\pi_3)$	5.89	2	38	58		2	8.15
$7b_2(n_-)$	6.51	2	74	11		13	9.10
$8a_1(n_+)$	7.37	2	76	10		12	10.06
$2a_2(\pi_2)$	8.78	0	63	19		18	11.5
$1b_1(\pi_1)$	9.55	1	35	25		39	(12.2)
q		+0.64	−0.62	+0.37 −0.28		−0.01	
F$_2$BAA							
$6b_1(\pi_3)$	7.83	1	35	56	6	1	9.85
$8b_2(n_-)$	8.97	3	67	12	5	13	11.34
$5b_1(F)$	9.64	2		5	92	2	12.6
$3a_2(F)$	9.71		13	5	77	5	.
$11a_1(F)$	10.10	3	26	4	60	5	.
$7b_2(F)$	10.37	5	12	5	76	2	.
$2a_2(\pi_2)$	10.97		46	6	21	27	13.5
$10a_1(n_+ + F)$	10.98	5	45	18	25	1	
$4b_1$	11.04	2	23	14	19	41	
q		+0.87	−0.51	+0.36 −0.20	−0.37	+0.08	

$11a_1$ (26%) and $10a_1$ (45%) MOs. In accordance with the calculated sequence of the levels in the approximation of Koopmans' theorem, the third band in the spectrum of F$_2$BAA should consequently be attributed to the states of ions with vacancies at the antibinding $F2p$ orbitals. In our first works devoted to investigating β-diketonate complexes of boron difluoride by UPS, we attributed the band at 12.8 eV to the n_+ orbital not allowing such a low IE for the F$_2$B group [6, 7]. Indeed, the IEs for $F2p$ electrons lower than 13 eV are characteristic of only metal fluorides with a prevalence of ion bonding [3].

The contradiction between the calculated results and the values of IE($F2p$) is explained first by Koopmans' defect for the levels of $F2p$ type exceeding the corresponding value for n orbitals of oxygen by 1.0–1.5 eV, and second by the influence of the molecular potential on the energies of $F2p$ electrons. Two oxygen atoms in the first coordination sphere of boron have negative charges higher than those of the fluorine atoms ($-0.51e$), due to the carbon atoms of carbonyl rather than the donor properties of boron. We can use the regularities in the UPS spectra of similar chelate complexes of metals to evaluate the IE of the n_+ orbital. The IEs for the wide series of β-diketonates of metametals that have noticeable covalent components

of the bonds [3, 9] allow us to estimate the energy range between IE(n_-) and IE(n_+) as 1.2–1.4 eV.

To evaluate the dependence of δ_A on the character of the MO of the F$_2$BAA complex, we compared the vertical IEs published in [3, 4, 9, 10] with our calculated values ε_i for the following compounds: BF$_3$, BF$_2$CH$_3$, CH$_2$=CF$_2$, benzene and its derivatives C$_6$H$_{6-n}$R$_n$ ($n = 1, 2$; R = F, CH$_3$), and complexes M(AA)$_n$ ($n = 1, 2, 3$).

Figure 1 shows our interpretation of the PE spectrum of F$_2$BAA, based on the calculated results and corrected for Koopmans' defects and the accepted value of $\Delta n = 1.3$ eV. In the left part of the diagram, we present the calculated energies for the ten upper MOs (A). The energies of levels B are corrected according to the results from estimating quantities δ_A for orbitals π_3 (δ_C), n_0(δ_O), and $F2p$ (δ_F). For the UOMO, the correction δ_C is 2.0 eV; for n_- and n_+ orbitals, $\delta_O = 2.4$ eV; while for the levels with the prevalent contribution of $2p$ AO of fluorine, $\delta_F = 3.4$ eV. Considering the dependence of Koopmans' defect on preferential MO localization led to inversion of the $F2p$ and n_+ levels. Consequently, the low-energy threshold of the third broad band is due to an MO with a predominant contribution of n_+ rather than to the fluorine electrons. The overlapping bands of the four electron pairs localized preferentially on the fluorine atoms thus follow.
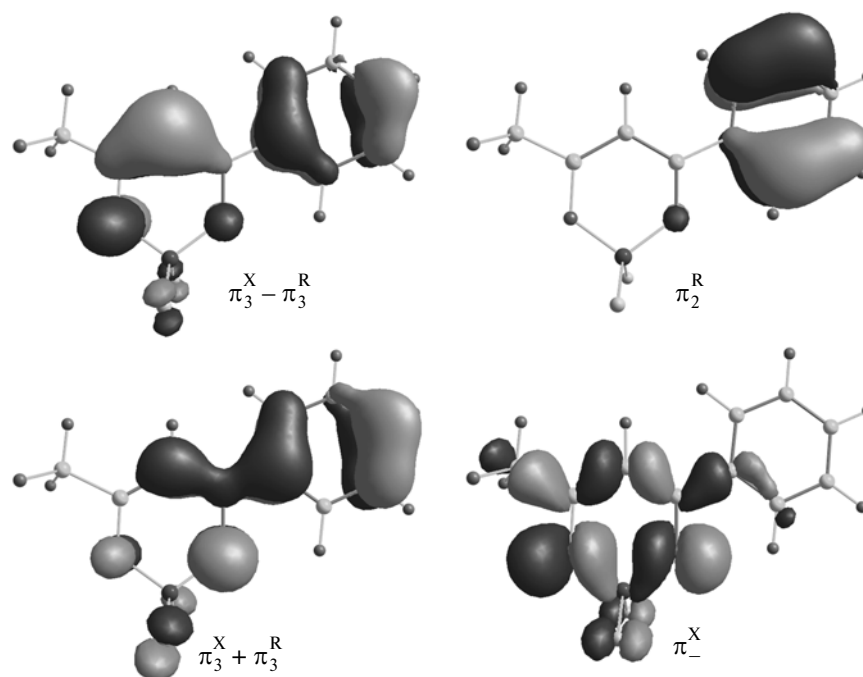
$\pi_3^X - \pi_3^R$

π_2^R

$\pi_3^X + \pi_3^R$

π_-^X

Fig. 3. Forms of the four upper MOs for compound II.

From the viewpoint of participation in covalent binding, the broad asymmetric contours of the first and second bands in the spectrum of F_2BAA with full width at a half maximum of 0.6 eV indicate considerable variation in the ion geometry upon the removal of electrons from weakly bound MOs. To establish the variations in the ion geometry in the ground state, we calculated the ionization energy as the difference between the total energies of the final and initial states with the frozen geometry of a neutral complex (IE_v), allowing for the optimization of the ion geometry (IE_a). The calculated values (9.99 and 9.69 eV) are close to the experimental ones (9.85 and 9.30 eV).

As a result of relaxation of the nuclear skeleton due to the removal of the electron from the π_3 UOMO, the lengths of the B−O and C1−C3 bonds increase by 0.06 Å. This MO is binding for these bonds, while a

Table 3. Electron density for atoms in the F_2BAA neutral complex and in the ionized state

Atom	F_2BAA	F_2BAA^+	Δe
F	9.37	9.30	0.07
B	4.13	4.07	0.06
O	8.51	8.40	0.11
C_β	5.63	5.58	0.05
C_γ	6.20	6.10	0.10
CH_3	8.92	8.77	0.15
H	0.80	0.72	0.08

decrease in the antibinding character for the B−F and O−C bonds leads to an increase in the order of the bonds and a reduction in R_{AB} (Table 1, Fig. 2). Among the angles between the bonds, the largest variations are characteristic of the angles in the coordination sphere of the boron atom. Substantial variations in the equilibrium values of the coordinates of the valence and deformation oscillations in the ion according to the Frank−Condon principle lead to an excess of 0.55 eV in the energy of the vertical transition, relative to IE_a. Electron relaxation in the ion leads to a reduction in the electron density for all atoms of the complex, including the methyl groups; but the largest variation is observed for the O and C3 atoms (Table 3), which make the greatest contribution to the UOMO.

In the complex of boron fluoride benzoylacetonate (F_2BBA), which (according to the calculated data) has a planar structure, the three upper occupied MOs in the conjugated π system are due to the interaction of the π_3 F_2BAA orbitals and upper degenerate in benzene e_{1g}. The first three bands in the PE spectrum and the values of ε_i allow us to estimate the result of the delocalization of π electrons and the total transfer of electron density. According to the calculated data, the antibinding combination of the π_3 MO of the chelate cycle with one of the two orbitals of C_6H_5 into which the $e_{1g}(b_1 + a_2)$ orbital is split is localized preferentially on the chelate cycle (67%), while the binding one has the close contributions of two cycles (Table 4, Fig. 3). The second component of the π orbital degenerate in benzene does not mix with the π system of the chelate cycle by virtue of symmetry. The energy range

between two delocalized orbitals (no. 54 and no. 52), 0.76 eV, is narrower than the experimental value of 0.91 eV, estimated from the PE spectrum expanded into Gaussians (Fig. 4, Table 5).

The positive induction effect of the phenyl group, which is due to a total loss of $0.18e$ in the electron density, is confirmed by a decrease of 0.2 eV in $IE(n_-)$ and a 0.56 eV increase in $IE(a_2)$ for the substituent relative to benzene. Above 11.5 eV, the overlap of the bands of the ion's energy states that correspond closely to the electron levels of the σ and π types of the phenyl group (orbitals e_{2g} and a_{2u} in benzene [10]) with the bands of the states of the chelate cycle makes the spectrum unacceptable for interpretation.

The methyl group in the n location of the benzene cycle of the substituent (compound III) produces variations in the region of three first bands of the spectrum that agree well with the variations in the IEs of two upper π levels upon moving from benzene to toluene. In the limits of experimental accuracy, the value of IE_v for the $a_2(\pi_2)$ orbital with the node at the $C-CH_3$ bond is invariable, but for the upper $b_1(\pi_3)$ level, the effect of superconjugation lowers the IE_v by 0.52 eV [10]. A decrease in the IE of the upper MO of the substituent leads to a shift of the first and third bands for compound III relative to compound II by 0.22 and 0.20 eV, respectively, with a shift of the second band by 0.15 eV (Table 5). According to the calculated data, destabilization of three upper levels with respect to compound II is 0.21, 0.08, and 0.21 eV (Table 4). The second consequence of destabilizing the UOMO of the substituent was a redistribution of the contribution to the binding and antibinding combinations of the upper levels of the substituent and the chelate cycle. In contrast to F_2BBA, the chelate cycle in this compound makes a greater contribution to the binding MO (Table 4).

In the xylene molecule m-$C_6H_4(CH_3)_2$, both upper π orbitals interact with pseudo π orbitals of methyl groups, lowering the IEs to 8.56 and 9.05 eV [14]. In
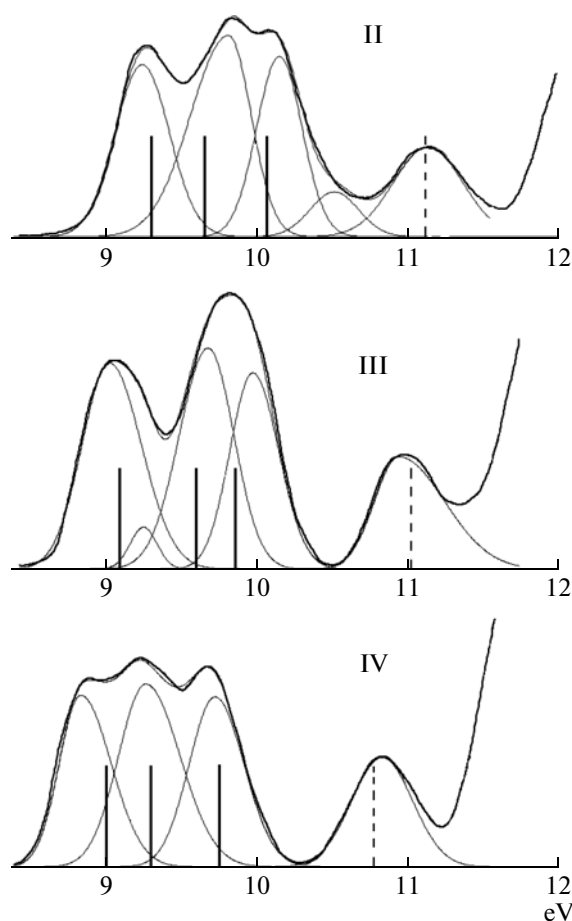

Fig. 4. Ultraviolet photoelectron spectra for compounds II–IV.

the PE spectrum of compound IV, destabilization of both upper MOs of the substituent relative to benzene leads to a shift of the three bands relative to compound II by 0.40, 0.55, and 0.43 eV (Table 5), while the contribution from the substituent to the UOMO rises to 63% (Table 4).

Table 4. Contributions from substituents and the chelate cycle to the three upper π orbitals of compounds II–IV, %

MO	AA	R_2	$-\varepsilon_i$, eV
Compound II			
54	67	33	7.40
53	0	100	7.77
52	49	51	8.16
Compound III			
58	46	54	7.19
57	9	91	7.69
56	55	45	7.95
Compound IV			
62	37	63	7.09
61	8	92	7.41
60	62	38	7.86

Table 5. Values of the IE determined by locations of the maxima of the bands in the spectra and by the results of expansion into Gaussians

MO	II		III		IV	
	IE	IE_g^*	IE	IE_g^*	IE	IE_g^*
$\pi_3^X - \pi_3^R$	9.25	9.25	9.03	9.02	8.86	8.85
π_2^R	9.80	9.82	9.77	9.67	9.22	9.27
$\pi_3^X + \pi_3^R$	10.15	10.16	9.98	9.96	9.65	9.73
n_-^X	11.13	11.14	11.04	10.93	10.81	10.83

The fourth band for three compounds is due to the n_- orbital, while the subsequent reduction in IE_v from 11.14 eV for compound II to 10.93 and 10.83 eV is due mainly to an increase in the electron density in the chelate cycle. In our approximation of the analysis of the distribution of the electron density according to Mulliken, the total transfer of the electron density from the aromatic substituent is 0.18e for compound II, 0.19e for compound III, and 0.23e for compound IV. The correlation of the MO energies presented in Fig. 4 (with the shift by quantities $\delta_C = 1.9$ eV and $\delta_O = 2.3$ eV) correlates well with the regularities in the PE spectra of complexes II–IV. Consequently, in the series of compounds II–III–IV, methylation of the phenyl group decreases not only the ionization energies of π-orbitals of the aromatic substituent, but also of the chelate cycle.

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