



Photoelectron spectra and electronic structure of some spiroborate complexes



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ABSTRACT

The electronic structure of the valence and core levels of three spiroborate complexes – boron 1,2-dioxyphenylene β -diketonates – has been investigated by methods of UV and X-ray photoelectron spectroscopy and quantum chemical density functional theory. The ionization energy of π - and n -orbitals of the dioxyphenylene fragment and β -diketonate ligand were measured from UV photoelectron spectra. This made it possible to determine the effect of substitution of one or two methyl groups by the phenyl in diketone on the electronic structure of complexes. The binding energy of nonequivalent carbon and oxygen atoms were measured from X-ray photoelectron spectra. The results of calculations of the energy of the valence orbitals of complexes allowed us to refer bands observed in the spectra of the valence electrons to the 2s-type levels of carbon and oxygen.

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1. Introduction

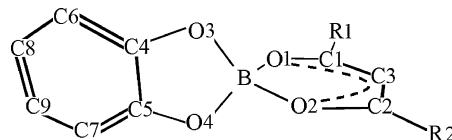
Modern chemistry of boron organic compounds is primarily associated with borane chemistry, the study of which is explained from both the theoretical (multi-centre bonds, clusters) and practical (fuel, neutron capture, radiotherapy) points of view [1]. However, other classes of boron compounds have attracted the attention of researchers. These include, in particular, spiroborate complexes, which are relatively easily synthesized [2,3] and sufficiently stable and have a crystal structure and high melting points. Chromophoric fragments of spiroborate complexes are not conjugated to each other. In this regard, study of the electronic structure and optical properties of these compounds is also interesting [4,5].

The determination of the relationship between the functional characteristics of the substances and their electronic structure provides opportunities for the directed synthesis of new compounds with desired properties. The most complete information about the electronic structure of the complexes can be obtained by the joint application of experimental and theoretical methods.

Previously, we have reported the results of research on the electronic structure of boron difluoride β -diketonates containing aromatic substituents with one [6] and two [7] benzene rings in β -positions by methods of ultraviolet photoelectron spectroscopy

(UPS) of vapour and density functional theory (DFT). Boron difluoride dibenzoylmethanate (F_2BDbm) has been studied by UPS, X-ray photoelectron spectroscopy (XPS), and X-ray emission spectroscopy [8,9]. As noted in [6–8], the DFT method make it possible to calculate the energy of the ionized states of the boron β -diketonate complexes with high accuracy. This is a good theoretical basis for the unambiguous interpretation of the photoelectron spectra and analysis of the structure of the valence electron levels.

This paper presents the results of a study of the electronic structure of acetylacetonate (I), benzoylacetonate (II), and dibenzoylmethanate (III) of boron 1,2-dihydroxyphenylene, as obtained by UPS, XPS, and DFT.



(I) $R_1 = R_2 = Me$

(II) $R_1 = Me$; $R_2 = Ph$

(III) $R_1 = R_2 = Ph$

2. Experimental and calculation methods

Spiroborate complexes I–III were obtained by the reaction of 2-*n*-butoxy-1,2,3-benzodioxaborol with β -diketonates according to [1]. UV-photoelectron spectra were registered by serial electron spectrometer ES-3201 with a monochromatic radiation source,

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He-I ($h\nu = 21.2$ eV). The determination accuracy of band maxima was under 0.02 eV. The temperature in the ionization cell was 200 to 240 °C. The X-ray photoelectron spectra of compounds I and III in condensed state were measured using an MXPS XP high vacuum double-chamber system (manufacturer—Omicron, Germany) with a hemispherical electrostatic analyser. The radiation energy was 1253.6 eV (Mg $K\alpha$). The spread function of the spectrometer in the mode of characteristic atomic level registration, which had been determined from the Ag3d_{5/2} band shape, had a half-width of 1.2 eV. Electron binding energy calibration (E_b) was performed based on the intrinsic standard method with the C1s carbon level as a mark. Purification of samples was done by repeated recrystallization. While estimating the atomic concentration of elements in a sample, we took into account relative ionization cross-sections and electron escape depth. The relative concentration of elements obtained from the intensities of the bands corresponding to 1s-electrons coincided with that calculated within the error of the method (10%).

All calculations were performed using the Firefly 7.1.G program package [10]. In the DFT method, a hybrid exchange–correlation functional B3LYP5 and basis set def2-TZVPP have been used [11,12]. Our choice of the basis set and functional for calculation of the electronic structure of β -diketonate complexes, including boron, has been justified by test calculation in [13] and successful application of theoretical models for the interpretation of the electron spectra [6–8,14,15]. In order to check the correspondence between optimized structures and local minimum points on a surface of potential energy, calculation of a Hessian matrix was performed. The absence of imaginary frequencies in vibration spectra points toward real minima on the potential energy surface.

For comparison of the experimental values of vertical ionization energies (IE) with energies of Kohn–Sham orbitals, ε_i , we used an expanded version of Koopmans' theorem:

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

where IE_i is the calculated ionization energy; $-\varepsilon_i$ is the Kohn–Sham one-electron energy; δ_i is the Koopmans defect, which is constant for a given type of MO energy correction.

The IE_i value corresponds to the energy of the Gaussian maximum, IE_g . The Gaussian maximum position for three higher electron levels is consistent with experimental ionization energies. UV bands corresponding to several orbitals were decomposed into Gaussians, taking into account the energy intervals between calculated electron levels.

The Koopmans defect δ_i is a measure of the deviation of calculated one-electron energies ε_i from the experimental vertical IE_i , that is, a measure of the violation of Koopmans' theorem. That is why Koopmans defect analysis is a useful tool as a theoretical approximation of quantum chemistry to describe the energy of ionic states of molecules. When taking into account the dependence of the amendment to the orbital energy δ_i on the nature of the electronic level, Koopmans' theorem makes it possible to obtain a good agreement between the experimental energy IE_i and the calculated energy ε_i of the Kohn–Sham molecular orbital (MO) [13,14,16].

3. Results and discussion

According to the calculation results, the geometry of compound I corresponds to the symmetry group C_{2v} (the planes of the chelate ring and fragment PheO₂B are perpendicular to each other).

Under substitution of one methyl group in compound I by phenyl (compound II), axis C_2 of fragment PheO₂B deviates by an angle of 15° relative to the plane of the chelate ligand, and in complex III this angle increases to 19°. Coplanarity of the planes of chelate and benzene rings is absent for compounds II and III, and

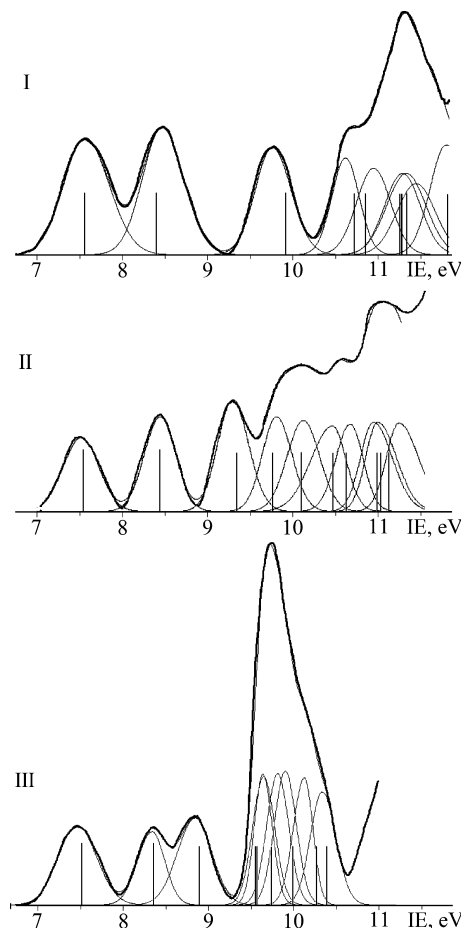


Fig. 1. Ultraviolet photoelectron spectra of the vapours of compounds I–III: experimental spectrum (heavy line), Gaussian components (thin envelope line), and calculated energies of molecular orbitals shifted by the value of Koopmans' defect (vertical lines).

the dihedral angles are 12° and 14°, respectively. According to the calculated results, compound III has symmetry C_s , but for convenience of comparison among MOs I–III we use the notation of the symmetry group C_{2v} in Table 3, Figs. 2 and 6. The usage of C_{2v} symmetry is justified by the inconspicuous difference between the total energies of the structures with C_s and C_{2v} symmetries (84 cm^{−1}).

For compounds I–III, the interatomic distances B–O3 and B–O4 (1.44 Å) are much smaller than the distances B–O1 and O2–B (1.52 Å). Also, for compounds I–III, small differences in the relevant interatomic distances (≤ 0.02 Å) and angles between bonds within the chelate ligand and dioxyphenylene fragment ($\leq 2^\circ$) were observed.

Fig. 1 shows the UV-photoelectron spectra of the vapours of the compounds studied. Under the decomposition of the spectral bands into Gaussian components, we took into account the number of calculated electronic levels, the energy intervals between them, and the closeness values of the ionization cross-sections of the electronic levels.

The images of the molecular orbitals of complexes I and III which are the most important for interpretation of UV-photoelectron spectra are shown in Fig. 2. Tables 1–3 contain the results of calculation of the relative contributions of the 1,2-dioxifenylenefragment PheO₂B, chelate ring, and substituents R in the molecular orbitals. The predominant localization of the MO is designated by superscripts: “x”—on a PheO₂B fragment, “ β ”—on a β -diketonate ligand, and “R”—on the substituents CH₃ and C₆H₅.

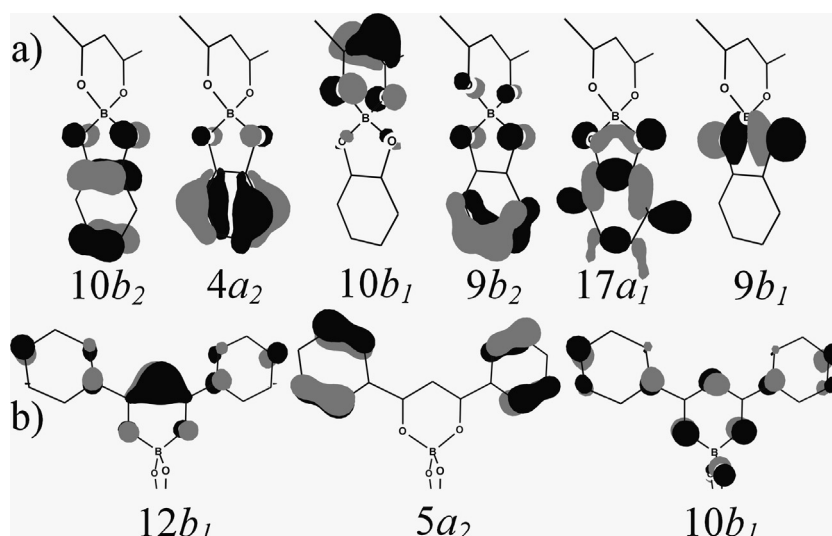


Fig. 2. Some molecular orbitals of compounds I (a) and III (b).

Table 1

Electron density localization (%), experimental and calculated energy levels (eV), and Koopmans defect of the compound I.

MO	Electron density localization			$-\varepsilon_i$	IE_g	δ_i
	PheO ₂ B/2O	HC(CO) ₂ /2O	2R			
10b ₂ (π_5^*)	99/22	1/1	0	5.23	7.56	2.33
4a ₂ (π_4^*)	99/11	1/0	0	6.07	8.47	2.40
10b ₁ (π_3^*)	6/4	92/30	2	7.61	9.76	2.15
9b ₂ (π_3^*)	88/20	10/8	2	8.42	10.63	2.21
17a ₁ ($\sigma^* - n_+^*$)	100/25	0/0	0	8.55	10.95	2.40
8b ₂ (n_-^*)	15/1	73/54	12	8.97	11.29	2.32
9b ₁ (n_-^*)	97/78	3/0	0	8.99	11.34	2.35
3a ₂ (π_2^*)	92/70	6/4	2	9.10	11.45	2.35
8b ₁ (σ^*)	99/13	1/0	0	9.51	11.81	2.30
16a ₁ ($\sigma^* + n_+^*$)	96/22	4/3	0	10.22	(12.5)	
15a ₁ (n_+^*)	15/2	75/51	10	10.61	(12.9)	
2a ₂ (π_2^*)	9/6	57/50	34	10.80	(13.1)	
7b ₂ (π_1^*)	80/31	8/5	12	11.12	(13.4)	

A correlation diagram of the upper π -, n -, and σ -MOs was built on the basis of calculations for compounds I–III and two previously investigated boron difluoride complexes [6,8] (Fig. 3).

Each of the first three bands in the UV-photoelectron spectra (Fig. 1) is caused by one-electron ionization processes. The first two

peaks in the spectra of compounds I–III are due to the two upper MOs of fragment PheO₂B— π_5^* and π_4^* , representing a combination of the top two antibonding π -orbitals of the phenylene rings ($1e_{1g}$ in benzene) and 2p π -orbitals of the oxygen. The third band corresponds to MO 10b₁ (π_3^*) of the chelate ring (compound I) or an antibonding combination of MOs π_3^* — π_3^* (compounds II and III) (Fig. 2). Unambiguous interpretation of the other bands is not possible without the results of quantum chemical modelling.

According to calculations that agree with the UV-photoelectron spectra, only two of the nine upper electronic levels of compound I with $IE < 12$ eV are located on the β -diketonate cycle (Fig. 3). An intense band with a maximum at 11.3 eV and a shoulder at 10.6 eV was decomposed into six Gaussian MOs in accordance with the calculated results. Among them, except for, as noted above, 8b₂ (n_-^*), are two π -orbitals, 9b₂ (π_3^*) and 3a₂ (π_2^*), and three MOs of n - and σ -type localized predominantly on PheO₂B (Fig. 2, Table 1). The overlap population of the two B—O bonds in PheO₂B (1.08), which exceeds the 35% overlap population of B—O bonds in the acetylacetonate ring (Table 4), is mainly realized by σ -orbitals 17a₁ and 9b₁ (Fig. 2).

Substitution of the methyl group by the phenyl one (compound II) leads to mixing of the orbitals (3^* and π_3^*). The theoretical energy interval between orbital 71 (3^* — 3^*) and bonding orbital 69 (3^* + 3^*) is 0.79 eV (Table 2). This is close to the experimental

Table 2

Electron density localization (%), experimental and calculated energy levels (eV), and Koopmans defect of the compound II.

MO number, type ^a	Electron density localization			$-\varepsilon_i$	IE_g	δ_i
	PheO ₂ B/2O	HC(CO) ₂ /2O	2R			
73, b ₂ (π_5^*)	99/22	1/1	0	5.19	7.52	2.33
72, a ₂ (π_4^*)	100/12	0/0	0	6.03	8.45	2.42
71, (3^* — 3^*)	4/2	62/16	34	7.25	9.29	2.04
70, (2^*)	0/0	1/1	99	7.69	9.81	2.12
69, (3^* + 3^*)	9/5	35/20	56	8.04	10.12	2.08
68, b ₂ (π_3^*)	87/20	10/8	3	8.39	10.46	2.07
67, a ₁ ($\sigma^* - n_+^*$)	99/25	1/1	0	8.51	10.67	2.16
66, (n_-^*)	20/6	67/50	13	8.90	10.94	2.04
65, b ₁ (n_-^*)	90/71	8/4	2	8.95	10.99	2.04
64, a ₂ (π_2^*)	91/69	5/3	4	9.09	11.24	2.15
63, b ₁ (σ^*)	98/12	1/0	1	9.49	(11.6)	
62, (σ^* — σ^*)	6/1	14/9	80	10.01	(12.1)	
61, a ₁ ($\sigma^* + n_+^*$)	92/21	1/1	7	10.20	(12.3)	
60, (σ^* + σ^*)	5/1	22/12	73	10.33	(12.4)	
56, b ₂ (π_1^*)	80/32	10/7	10	11.14	(13.1)	

^a For MO, localized predominantly on PheO₂B fragment, the C_{2v} symmetry is used.

Table 3

Electron density localization (%), experimental and calculated energy levels (eV), and Koopmans defect of the compound III.

MO	Electron density localization			$-\varepsilon_i$	IE_g	δ_i
	PheO ₂ B/2O	HC(CO) ₂ /2O _B	2R			
19b ₂ (π_5^*)	99/22	1/1	0	5.16	7.45	2.35
6a ₂ (π_4^*)	100/12	0/0	0	6.01	8.34	2.35
12b ₁ (3^* — 3^*)	1/1	53/10	46	6.99	8.85	1.86
5a ₂ (π_2^*)	0/0	1/1	99	7.62	9.64	2.02
11b ₁ (π_2^*)	0/0	1/1	99	7.62	9.65	2.03
4a ₂ (π_3^*)	3/1	13/10	84	7.79	9.82	2.03
10b ₁ (3^* + 3^*)	12/7	39/23	49	8.06	9.91	1.85
18b ₂ (π_3^*)	87/20	11/8	2	8.37	10.14	1.77
26a ₁ ($\sigma^* - n_+^*$)	99/26	1/1	0	8.48	10.34	1.86
17b ₂ (n_-^*)	16/2	70/53	14	8.88	(10.8)	
9b ₁ (n_-^*)	93/76	5/1	2	8.93	(10.9)	
3a ₂ (π_2^*)	91/68	5/2	4	9.09	(11.0)	
8b ₁ (σ^*)	99/11	1/0	0	9.47	(11.4)	
24a ₁ ($\sigma^* + n_+^*$)	93/22	1/1	6	10.17	(12.1)	
14b ₂ (π_1^*)	86/35	6/4	8	11.13	(13.1)	

Table 4

Effective charges (a.u.) of the fragments in NBO approximation and B–O, B–F bond orders.

Compound	Effective charge				Bond order	
	B	PheO ₂ /2O 2F	HC(CO) ₂ /2O	2R	B–O ₁	B–O ₃ B–F
PheO ₂ Baa (I)	+1.13	–0.94/–1.30	–0.29/–1.12	+0.10	0.80	1.08
PheO ₂ Bba (II)	+1.13	–0.95/–1.30	–0.31/–1.13	+0.13	0.79	1.07
PheO ₂ Bdbm (III)	+1.13	–0.95/–1.30	–0.33/–1.14	+0.15	0.80	1.08
F ₂ Baa	+1.21	–1.00	–0.31/–1.14	+0.10	0.77	1.15
F ₂ Bba	+1.21	–1.00	–0.33/–1.15	+0.12	0.77	1.15
F ₂ Bdbm	+1.21	–1.00	–0.35/–1.16	+0.14	0.77	1.17

value (0.83 eV). The orbital (2^R , which is degenerate with the upper (3^- -MO (ϵ_{1g})) of benzene, is between delocalized orbitals 71 and 69. According to the calculation results, the next six MOs' localizations and energies are close to the molecular orbitals $9b_2$ (π_3^x), $17a_1$ ($\sigma^x-n_+^x$), $8b_2$ (n_-^{β}), $9b_1$ (n_-^x), $3a_2$ (π_2^x), and $8b_1$ (σ^x) of compound I (Table 1).

A broad band with a maximum at 9.7 eV in the UV-photoelectron spectrum of compound III is due to the photoionization processes of the six electronic levels. According to the calculation, the first three bands under the decomposition into Gaussian components correspond to three π -orbitals of the phenyl groups, and the fourth one—corresponds to the orbital $10b_1$ ($(3^R + 3^{\beta})$). A shoulder at 10.3 eV is due to two MOs, $18b_2$ (π_3^x) and $26a_1$ ($\sigma^x-n_+^x$), of fragment PheO₂B (Fig. 1, Table 3).

For orbitals π_5^x and π_4^x , localized on a fragment PheO₂, Koopmans' defect δ_i in the order I–II–III varies slightly (the average value for the three compounds is 2.36 eV). For other levels, due to increased relaxation correction in the final state under substitution of the CH₃ group by C₆H₅, the average value of δ_i decreases. For compounds I, II, and III, the average values δ_i are 2.30, 2.09, and 1.92 eV with an average deviation of levels of 0.07, 0.04, and 0.09 eV, respectively. On matching the calculated energies to the

experimental spectra the scale $-\epsilon_i$ was shifted by 2.36 eV for the top two MOs. For the next levels, the shift was assumed to be equal to δ_i for every compound. Thus, the Kohn–Sham MO calculated energies reproduce the order of the orbital IE and the energy intervals between levels within the error of 0.1 eV. For deeper MOs, the IE values were estimated with an accuracy of 0.1 eV from ϵ_i and δ_i (Tables 1–3).

For compound I, $IE_3 = 9.76$ eV (π_3^{β}) and $IE_6 = 11.29$ eV (n_-^{β}) (Table 1), coinciding with the corresponding values of IE in the UV-photoelectron spectrum of boron difluoride acetylacetonate F₂Baa (first two bands) with an accuracy of 0.1 eV [6]. A similar coincidence of the values of IE was also found for the top three levels of β -diketonate ligand in compound II (Table 2) and boron difluoride benzoylacetonate F₂Bba [6]. Minor changes of ϵ_i values for π -MO under substitution of two fluorine atoms by PheO₂ group are seen on the correlation diagram of calculated orbital energies of compounds I–III, boron difluoride benzoylacetonate F₂Bba, and boron difluoride dibenzoylmethanate F₂Bdbm (Fig. 3). Low sensitivity of the calculated and experimental energy of levels π_3^{β} , n_-^{β} , and π^R to substitution of two acceptor atoms F by the aromatic group PheO₂ is explained by similar values of effective charges in the β -diketonate ligand. The total effective charges of atoms of β -diketonate ligand in complexes of boron difluoride and compounds I–III differ by 0.02 a.u. according to the calculations in the approximation of natural bonding orbitals (NBOs) (Table 4). The correlation diagram also shows the weak energy sensitivity of seven higher levels of PheO₂B fragment in the order I–II–III under substitution of methyl groups by the phenyl ones.

More than 80% of the electron density lost by the boron atom through the formation of chemical bonds is localized on the PheO₂ group, which affects the energies of the core electrons (Table 4).

The calculated energies determining the half-width and position of the band maxima in the scale of binding energies (E_b) are plotted on the X-ray photoelectron spectra of C1s- and O1s-electrons of compounds I and III (Fig. 4). For C1s-electrons in compound I,

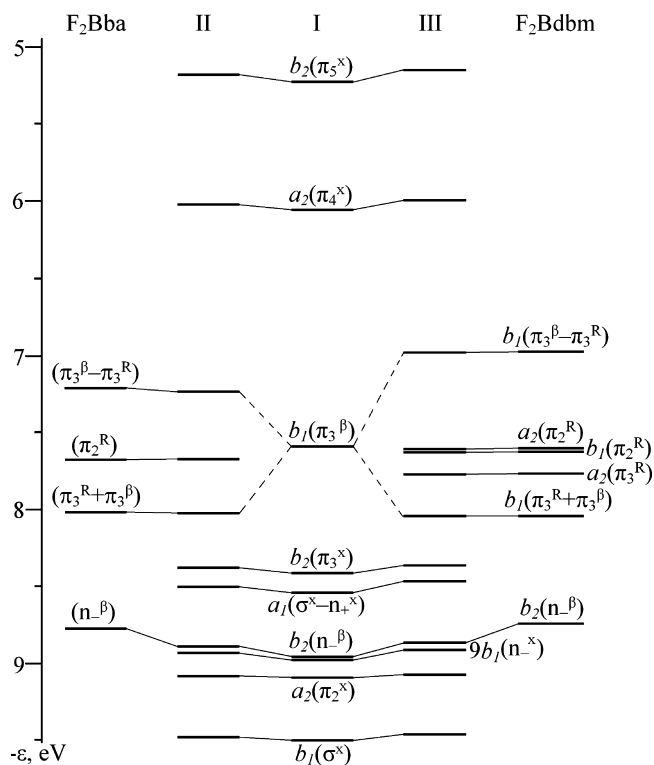


Fig. 3. The correlation diagram of the upper π - and σ -MOs of the compounds I–III, boron difluoride benzoylacetonate (F₂Bba), and boron difluoride dibenzoylmethanate (F₂Bdbm).

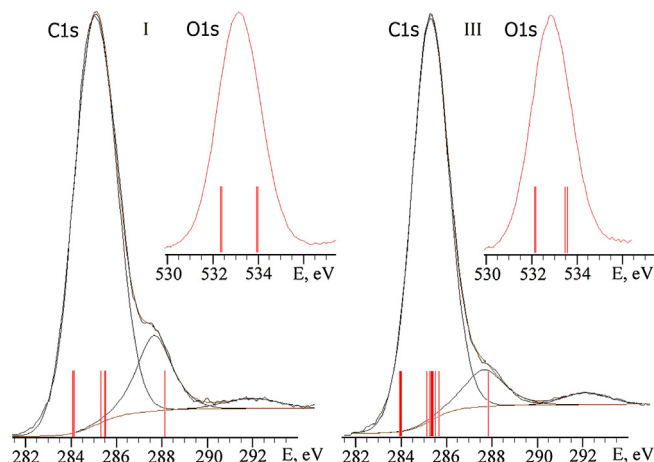


Fig. 4. X-ray photoelectron spectra of C1s- and O1s-levels of compounds I and III.

Table 5

Binding energies E_b and half-widths (eV) of bands in X-ray photoelectron spectra of 1s-electrons of compounds I, III, and F₂Bdbm.

Compound	PheO ₂ Baa		PheO ₂ Bdbm		F ₂ Bdbm [8]	
	E_b	Half-width	E_b	Half-width	E_b	Half-width
C1s	285.0	2.2	285.3	1.9	285.5	1.6
C1s(C _β)	287.7	1.8	287.7	2.1	288.0	1.8
O1s	533.0	2.2	533.2	2.1	533.7	1.9
B1s	193.1	1.7	193.3	1.7	194.6	1.5

the low-energy group of levels is conditioned by the atoms C₆–C₉ of the phenylene ring. The levels of the two carbonyl carbon atoms are shifted by 4 eV, while the central group of levels corresponds to the remaining five carbon atoms. The overlapping bands of two groups of levels in the E_b range of 284–286 eV caused an FWHM of 2.2 eV for the total band with its maximum at 285.0 eV (Table 5). Atoms of two C₆H₅ groups in compound III increased the number of levels in the second group up to 11, thereby reducing the bandwidth at half maximum to 1.9 eV. When determining the value of E_b (C1s)=285.3 eV we considered, as well as for F₂Bdbm [8], the growth of the values of IE of π -electrons of the phenyl groups from 9.24 eV in the benzene molecule [19] to 9.64 eV for compound III (Table 3). On the basis of the shift of the valence π -electrons the table value of E_b (C1s) for benzene in the condensed state 284.9 eV [20] increased by 0.4 eV. The FWHM for O1s-electrons (2.2 eV) is caused by the splitting (according to calculation) of the energies of atoms O1 and O2 of the beta-diketonate group and atoms O3 and O4 of the PheO₂ group (Fig. 4).

There are five overlapping bands in the X-ray photoelectron spectra of the valence band of the complexes I and III (Fig. 5). The relative intensities and the shapes of the bands depend on the distribution of electronic density and the relative ionization cross-sections of 2s- and 2p-levels (σ_s , σ_p). For Mg K α radiation, the calculations determined the ratio of σ_s : σ_p for carbon is 26, and for oxygen is 12 under σ_p (C): σ_p (O) is 1:6 [18].

As shown in [8], the intensive bands in the spectrum of F₂Bdbm in the E_b range from 10 to 21 eV correlate with benzene MOs 2a_{1g}, 2e_{1u}, 2e_{2g}, and 2b_{1u}. Hereafter in the text and tables, these orbitals are denoted as α , e_1 , e_2 , and b .

In the range of ionization energies of 25.9 eV (2a_{1g}) to 17.4 eV (2b_{1u}), the energy intervals of 3.4, 3.3, and 3.8 eV [19,21] are well reproduced in the spectra of compounds containing phenyl groups.

Table 6 shows the energies and localization of lower valence s-type MOs of chelate and benzene rings for compounds I and III. A predominant localization of the main part of the valence MOs on one of the chelate groups makes it possible to split orbitals (in the scale of calculated energies) into two rows for compound I and three rows for compound III (Fig. 5).

The intensive band 5 in the spectra of both complexes is explained by two pairs of electronic levels localized predominantly (up to 80%) on the oxygen atoms (Table 6, Fig. 6). The half-width of this band (4.7 eV) is in good agreement with the theoretical estimation of energy splitting of four MOs (3.46 eV).

Band 4, with a peak at 17.7 eV and bend 4' at 19.8 eV, is caused by electrons of three C2s-levels of acetylacetonate ligand – 3a₁, 2b₂, and 5a₁ – and three levels of the C₆H₄ ring – 4a₁(α), 2b₁(e_1), and 6a₁(e_1).

The narrow band 3 at 14.5 eV in the E_b range of 13–15 eV may be exactly attributed to the two levels of the C₆H₄ group – 8a₁(e_2) and 3b₁(e_2) – and the 3b₂ (C β) level of the diketonate ligand. The less intensive band 2 at 11.3 eV corresponds to the top of the six molecular orbitals of s-type of the C₆H₄ group.

The first broad band with bends 1' and 1'' corresponds to ionization of 22 p-type MOs including four n-orbitals of oxygen and eight

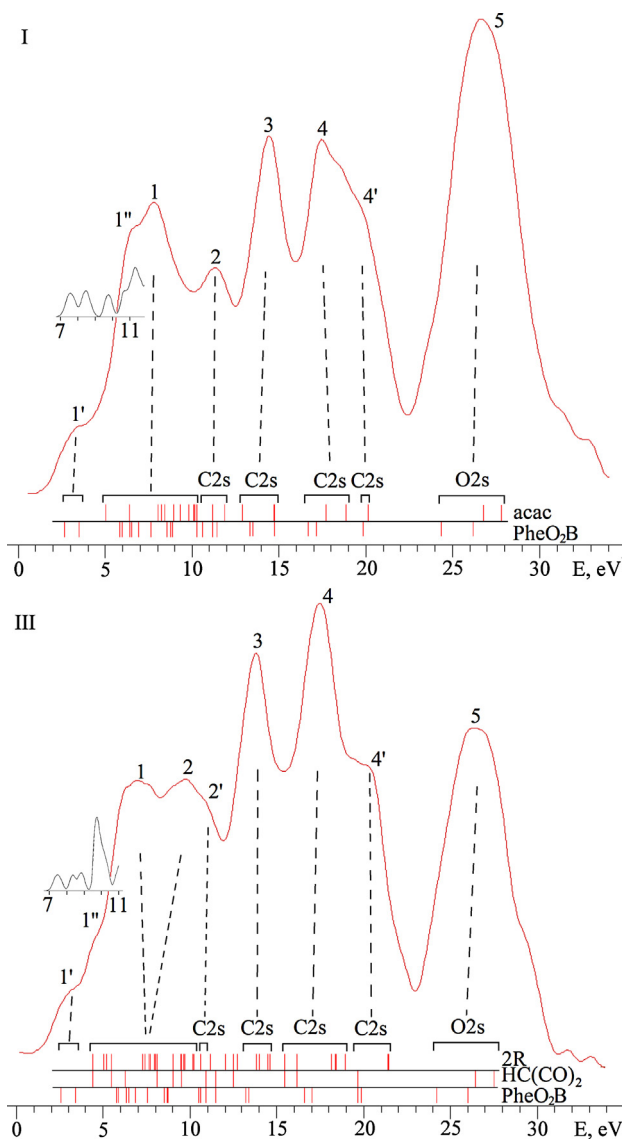


Fig. 5. X-ray and UV photoelectron spectra of valence levels of compounds I and III.

π -orbitals. The first two bands in the UV-photoelectron spectrum of vapour (Fig. 1) appeared in the X-ray photoelectron spectrum of the condensed state in the form of bend 1' near the top of the occupied band. An intensive peak at 11.3 eV (referred to six states in Table 1) corresponds to bend 1''. Comparison of the UV-photoelectron spectra and X-ray photoelectron spectra of valence electrons confirms this conclusion.

The substitution of two CH₃ groups by C₆H₅ groups in compound III increases the number of electron levels in the valence band from 41 to 63, including the s-type levels from 16 to 26. Since the number of oxygen atoms did not change, the relative intensities of bands 1–4 in the spectrum increased (Fig. 5). As shown in Table 6, bend 4' and peak 4 correspond to the electron levels α and e_1 of three benzene rings and atoms C1–C2–C3 (C β). Three pairs of e_2 orbitals (Fig. 6b) caused band 3, and the overlapping bands 1 and 2 correspond to 38 levels of p-type of PheO₂, dbm groups, and three 2s(b)-levels of benzene rings. Bend 1' (as for the spectrum of compound I) corresponds to the first two bands in the UV-photoelectron spectrum of vapour and the weak bend 1'' corresponds to the intensive band at 9.8 eV in the spectrum of vapour.

Table 6
Localization (%) and calculated energies (eV) of 22 lower valence MOs of compounds I and III.

Compound I						Compound III					
Band	MO	Localization			$-\varepsilon_i$	Band	MO	Localization			$-\varepsilon_i$
		HC ₃ O ₂	2R	PheO ₂ B				HC ₃ O ₂	2R	PheO ₂ B	
5	1a ₁	90	0	10	30.40	5	1a ₁	87	0	13	30.18
	1b ₂	97	1	2	29.37		1b ₂	96	2	2	29.11
	2a ₁	7	0	93	28.78		2a ₁	9	0	91	28.68
	1b ₁	0	0	100	26.94		1b ₁	0	0	100	26.86
4'	3a ₁ (C ^β)	60	16	24	22.72	4'	3a ₁ (a)	5	95	0	24.11
	4a ₁ (a)	17	4	79	22.42		2b ₂ (a)	0	100	0	24.06
4	2b ₂ (C ^β)	37	62	1	21.45		4a ₁ (a)	29	16	55	22.52
	5a ₁ (C ^β)	44	55	1	20.30		5a ₁ (C ^β)	35	18	47	22.31
	2b ₁ (e ₁)	0	0	100	19.73	4	3b ₂ (e ₁)	19	80	1	21.58
	6a ₁ (e ₁)	4	2	94	19.26		6a ₁ (e ₁)	6	94	0	21.06
3	7a ₁	53	12	35	17.33		4b ₂ (e ₁)	1	99	0	21.01
	3b ₂ (C ^β)	59	35	6	17.30		7a ₁ (e ₁)	27	73	0	20.79
	8a ₁ (e ₂)	1	0	99	16.09		2b ₁ (e ₁)	0	0	100	19.67
	3b ₁ (e ₂)	3	0	97	15.92		8a ₁ (e ₁)	7	2	91	19.22
2	5b ₂	79	10	11	15.49		5b ₂ (C ^β)	44	54	2	18.80
	9a ₁	81	16	3	14.46		9a ₁ (C ^β)	34	49	17	18.09
	10a ₁	16	8	76	14.02	3	6b ₂ (e ₂)	6	93	1	17.24
	4b ₁ (b)	38	11	51	13.75		10a ₁ (e ₂)	8	90	2	17.10
1	11a ₁	0	0	100	13.18		11a ₁ (e ₂)	25	54	21	16.62
	5b ₁	21	34	45	12.85		7b ₂ (e ₂)	22	74	4	16.46
	1a ₂	38	62	0	12.74		12a ₁ (e ₂)	2	2	96	16.02
	6b ₂	49	46	5	12.67		3b ₁ (e ₂)	8	1	91	15.84

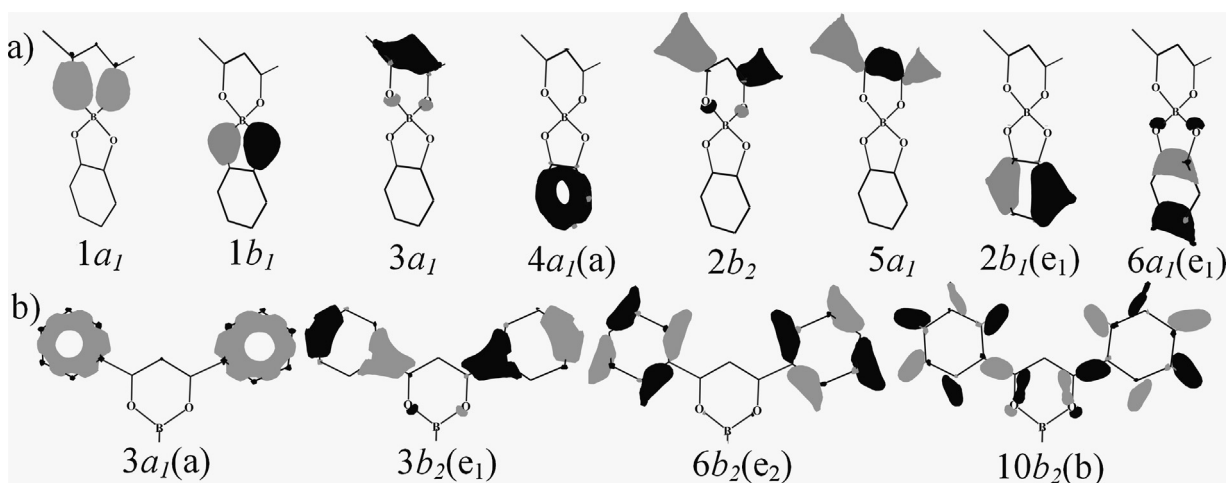


Fig. 6. The distribution of electronic density on some lower valence levels of compounds I (a) and III (b).

4. Conclusion

For three spiroborate complexes (boron 1,2-dioxyphenylene β -diketonates), it was determined by UV-photoelectron spectroscopy of vapour and density functional theory that the two top electron levels were localized on the 1,2-dioxyphenylene fragment PheO₂. Substitution of CH₃ groups by C₆H₅ ones in the β -diketonate complexes did not strongly effect the energy and localization of the two upper as well as the deeper π - and σ -orbitals of PheO₂. Besides, the substitution of two fluorine atoms by PheO₂ groups in boron difluoride β -diketonates F₂Bba and F₂Bdbm did not affect on the energy or the composition of π -levels of β -diketonate ligands. An absence of mutual disturbance of the electron levels of the two chelate rings binding with the boron atom (determined by experimental and theoretical methods) is explained by the orthogonality of their planes in spiroborate complexes.

The structure of X-ray photoelectron spectra of the valence electrons is in good agreement with the energies and composition (contribution of O2s and C2s) of Kohn–Sham orbitals.

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