

## PHOTOELECTRON SPECTRA AND ELECTRONIC STRUCTURE OF BORON DIPROPYL IMIDOYLAMIDINATES

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UDC 544.15:544.17:544.18

The electronic structure of seven boron dipropyl imidoylamidinates is studied by ultraviolet photoelectron spectroscopy and density functional theory. The effect of different substituents at carbon and nitrogen atoms of the chelate ring on the nature and sequence of electronic levels is determined. Unlike their  $\beta$ -diketonate analogues, for nitrogen-containing compounds the absence of a noticeable mixing of orbitals of the  $\pi$  benzene and chelate rings is revealed. It is shown that in the energy range up to 10 eV the calculated results corrected for the Koopmans defect reproduce well the energy ranges between the ionized states of the complexes.

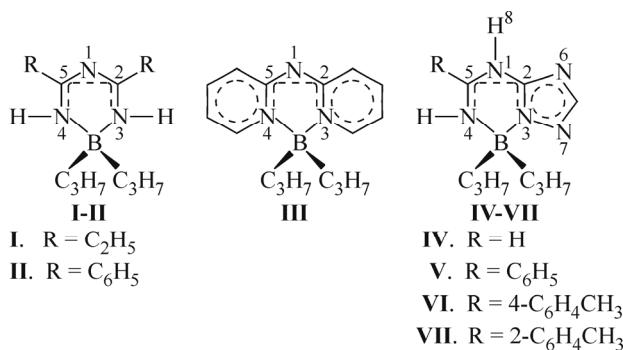
**DOI:** 10.1134/S0022476615030063

**Keywords:** electronic structure, photoelectron spectroscopy, density functional theory, Koopmans theorem, nitrogen-containing boron complexes, imidoylamidinates,  $\beta$ -diketonates.

### INTRODUCTION

Boron  $\beta$ -diketonates  $X_2B(O-C(R_1)-C(R_2)-C(R_3)-O)$  exhibiting intensive luminescence [1-4] and high biological activity [5, 6] attract great attention of researchers. Luminescent [7] and antiviral properties [8] of nitrogen analogues of boron  $\beta$ -diketonates determine the relevance of investigations of complexes with B–N bonds.

The occurrence of the relationship between the physicochemical properties of compounds and their electronic structure governs the importance of studying the electronic structure of boron complexes. The establishment of the “structure–property” dependences in series of compounds makes it possible to perform a directed synthesis of chelates with the desired properties, including intensive luminescence [2].



In this work we report the results of studies of the electronic structure of seven boron dipropyl imidoamidates. These compounds were synthesized in the Institute of Organic Chemistry, Russian Academy of Sciences, Moscow [9-11]. Ultraviolet photoelectron (UPS) spectra of complexes in the gas phase were measured in Far Eastern Federal University [12-14]. In [13] the interpretation of the spectra based on calculations in the semi-empirical MNDO/3 approximation is ambiguous and limited, which did not provide the information on the electronic structure of the complexes. The comparison of results obtained by UPSC and density functional theory (DFT) gives the unambiguous data on the electronic structure of compounds **I-VII**.

## EXPERIMENTAL AND CALCULATION PROCEDURES

UPS spectra were measured on an ES-3201 electronic spectrometer with a He **I** monochromatic radiation source ( $h\nu = 21.2$  eV). The systematic error in the determination of the energies of band maxima did not exceed 0.02 eV. The temperature of the ionization cuvette varied from 20 °C to 240 °C and depended on the sublimation temperature of the vapor of the sample under study.

Calculations were carried out using the Firefly 7.1.G program [18] with the hybrid exchange-correlation B3LYP5 functional [19] and the TZVPP basis set [20, 21]. The choice of the basis set and the functional for the calculation of boron compounds **I-VII** is caused by good correlation of the theoretical and experimental data in [16, 17, 22]. In order to assess the correspondence of the optimized geometry of molecules of **I-VII** to the local minimum points on the potential energy surface the Hessian matrix was calculated.

Based on the calculated data the regularities in the UPS spectra of the studied compounds are analyzed. In the UPS spectra, the bands corresponding to several orbitals fitted by Gaussians with regard to relative ionization cross-sections and the number of the calculated electronic levels. In the comparison of the experimental ionization energies  $IE_i$  (the  $IE_i$  values correspond to the energies of the  $IE_g$  Gaussian maxima) with the calculated Kohn–Sham orbital energies  $\varepsilon_i$  the extended variant of the Koopmans theorem was applied ( $IE_i = -\varepsilon_i + \delta_i$ ). With regard to the correction for the orbital energy  $\delta_i$  this theorem makes it possible to achieve good agreement between the experimental and calculated energies [15-17].

## RESULTS AND DISCUSSION

According to the calculated data, molecules of **I-III** are symmetric with respect to the twofold axis passing through B and N1 atoms. The total energy minimum of these molecules is observed when the  $C_2H_5$  moieties of the  $B(C_3H_7)_2$  complexing agent are located on both sides of the plane perpendicular to the chelate ring.

The replacement of ethyl groups at carbonyl carbon atoms by phenyl ones (complex **II**) does not result in noticeable changes in the geometric parameters of the chelate ring (Table 1). Dihedral angles between the planes of the chelate and benzene rings are 25°. In complex **III** three conjugated rings have a  $\pi$  system isoelectronic to the anthracene molecule, which causes a noticeable change in the geometric parameters of the central ring (Table 1). In particular, B–N and N–C bond lengths increase by 0.04 Å and 0.06 Å respectively.

**TABLE 1.** Interatomic Distances for Compounds **I-IV** and Effective Charges (NBO) on the Molecular Fragments of **I-II'**

Chemical bond	I	II	III	IV	Fragments	I	I'	II	II'
	$R_{AB}$ , Å					Effective charge, au			
B–N3	1,58	1,58	1,62	1,58	B	0,63	0,88	0,63	0,88
B–N4	1,58	1,58	1,62	1,63	2NH/2O	–0,54	–1,14	–0,50	–1,13
N3–C2	1,31	1,31	1,37	1,33	2C $\beta$	1,05	1,10	1,00	1,02
N4–C5	1,31	1,31	1,37	1,29	N1/C $\gamma$ H	–0,63	–0,28	–0,61	–0,23
C5–N1	1,34	1,34	1,33	1,34	2C <sub>3</sub> H <sub>7</sub>	–0,59	–0,63	–0,59	–0,63
C2–N1	1,34	1,34	1,33	1,40	2R	0,08	0,07	0,07	0,09

**TABLE 2.** Character and Symmetry of MOs, Electron Density Location (%), Calculated Electron Energy  $-\epsilon_i$ , Energy of Gaussian Maxima  $IE_g$  and Values  $\delta_i$  (eV) for Compounds **I-III**

Number, symmetry, and character of MOs	MO contribution			$-\epsilon_i$	$IE_g$	$\delta_i$	Number, symmetry, and character of MOs	MO contribution			$-\epsilon_i$	$IE_g$	$\delta_i$
	X <sub>3</sub>	$\beta$	2R					X <sub>3</sub>	$\beta$	2R			
Compound I							Compound II						
62, $b (\pi_3^\beta - \sigma''^X)$	48	51	1	5,76	7,75	1,99	86, $b (\pi_3^\beta - \sigma''^X)$	51	48	1	5,83	7,59	1,76
61, $a (n_N)$	8	87	5	7,34	9,41	2,07	85, $b (\pi_3^R)$	6	13	81	7,09	8,86	1,77
60, $b (\sigma'^X + \pi_3^\beta)$	57	40	3	7,57	9,66	2,09	84, $a (\pi_3^R)$	2	22	76	7,17	8,92	1,75
59, $a (\sigma'^X + n_N)$	82	17	1	7,72	9,87	2,15	83, $a (\pi_2^R)$	1	8	91	7,30	9,19	1,89
Compound III							82, $b (\pi_2^R)$	0	1	99	7,33	9,23	1,90
72, $B (\pi_7^\beta)$	8	92	–	5,33	7,05 7,25		81, $a (n_N)$	24	60	16	7,57	9,44	1,87
71, $B (\sigma''^X - \pi_6^\beta)$	70	30	–	6,99	8,87	1,88	80, $b (\sigma''^X + \pi_3^\beta)$	57	31	12	7,79	9,56	1,77
70, $a (n_N)$	6	94	–	7,24	9,24	2,00	79, $a (\sigma'^X + n_N)$	67	27	6	7,81	9,67	1,86
69, $a (\pi_5^\beta)$	1	99	–	7,48	9,49	2,01							

The interaction of the conjugated  $\pi$  systems of six- and five-membered rings (complexes **IV-VII**), containing three nitrogen atoms each, results in a noticeable asymmetry of the six-membered ring (Table 1). Unlike **I-III**, in compounds **IV-VII** the  $C_2H_5$  moieties of the propyl groups of the complexing agent are turned to one side relative to the C–B–C plane. The replacement of the hydrogen atom at the carbonyl carbon atom by the phenyl group and its derivatives causes minor changes in the bond lengths and bond angles in the chelate ligand. For **V**, **VI**, and **VII** the dihedral angles between the planes of the chelate and benzene rings are 40°, 38°, and 59° respectively.

In the text and Tables 2 and 3 the indices denote the dominant localization of the molecular orbitals (MOs): X on the  $(C_3H_7)_2B$  complexing agent;  $\beta$  on the ligand  $((NH)_2C_2N$ ,  $N_3C_2(C_4H_4)_2$ ,  $N_3C_3H_3$ ); R on the substituents ( $C_2H_5$ ,  $C_6H_5$ ,  $H$ ,  $2-C_6H_4CH_3$ ,  $4-C_6H_4CH_3$ ). For the  $BC_2$  bonding orbitals ( $\sigma^X$ ) the local symmetry  $C_s$  relative to the chelate ligand plane is used. The designation  $n_N$  is applied for the  $\sigma$ -type orbitals located mainly on the nitrogen atoms.

An analysis of the interaction between the  $\pi$ -system of the chelate ring and substituents in complexes **I-II** has shown the mixing of  $\pi_3^\beta$  and  $\sigma''^X$  orbitals (Table 2, Fig. 1). For compound **II** the noticeable mixing of  $\pi_3^\beta$  and  $\pi_3^R$  MOs is absent (Table 2). In complex **III** there are seven  $\pi$  orbitals of the conjugated rings and one pseudo- $\pi$  MO  $\sigma''^X$  (Table 2).

The comparison of the calculated parameters of the electronic structure of complexes **I-II** and their isoelectronic  $\beta$ -diketonate analogues **I'-II'** (with maintaining the initial geometry the CH group substitutes for the N1 atom and oxygen atoms for NH groups at positions 3 and 4) has shown that for compounds **I-II** the boron atom has a less positive charge and the NH group has a less negative charge than oxygen and boron atoms in complexes **I'-II'** (Table 1). Unlike its nitrogen analogue **II**, for compound **II'** a noticeable mixing of  $\pi_3^\beta$  and  $\pi_3^R$  MOs is observed.

As seen from the correlation diagram (Fig. 2) the five upper occupied MOs of complexes **IV-VI** have a similar character. The  $n_N$  orbital of compounds **IV-VII** is mainly located on the N6 and N7 atoms (Fig. 3). Methylation of the phenyl ring in the *ortho*-position (compound **VII**) substantially changes the characters and energies of the fourth, fifth, and sixth upper occupied MOs (Figs. 2 and 3). For compounds **IV-VII** the calculation has shown the considerable mixing of orbitals of the conjugated  $\pi$  systems of the five- and six-membered rings and  $\sigma''^X$  MO (Table 3, Fig. 3).

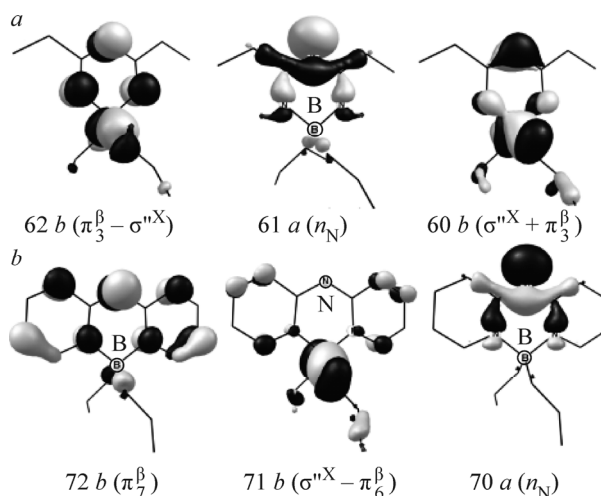
By analogy with **II**, for complexes **V-VII** the visible mixing of the ligand  $\pi$  orbitals and benzene ring MOs is absent (Tables 2 and 3). In the series of compounds **IV-VII** the electronic levels of the  $\pi_3^R$  MO are lower than the corresponding levels of complex **II** by 0.6-1.0 eV (Fig. 2, Tables 2 and 3). This is due to the field effect of the six-membered ring transferred the electron density to the five-membered ring (0.47 au).

**TABLE 3.** MO Character, Electron Density Location (%), Calculated Electron Energy  $-\varepsilon_i$ , Energy of the Gaussian Maxima  $IE_g$ , and Values  $\delta_i$  (eV) for Compounds **IV-VII**

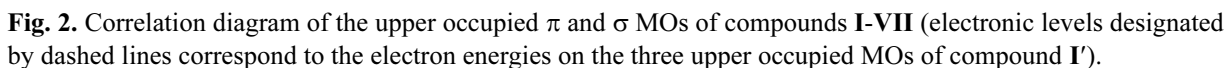
Number and character of MOs	MO contribution			$-\varepsilon_i$	$IE_g$	$\delta_i$	Number and character of MOs	MO contribution			$-\varepsilon_i$	$IE_g$	$\delta_i$
	X	$\beta$	R					X	$\beta$	R			
Compound IV							Compound V						
56, ( $\pi_5^\beta-\sigma''^X$ )	37	63	0	6,18	7,99	1,81	76, ( $\pi_5^\beta-\sigma''^X$ )	35	65	0	6,00	7,70	1,70
55, ( $\pi_4^\beta-\sigma''^X$ )	41	59	0	7,17	9,24	2,07	75, ( $\pi_4^\beta-\sigma''^X$ )	41	55	4	6,95	8,87	1,921
54, ( $n_N$ )	3	97	0	7,44	9,53	2,09	74, ( $n_N$ )	3	97	0	7,28	9,24	1,96
							73, ( $\pi_3^\beta+\sigma''^X$ )	32	66	2	7,61	9,45	1,84
							72, ( $\sigma'^X$ )	70	27	3	7,68	9,64	1,96
							71, ( $\pi_3^R-\sigma'^X$ )	29	10	61	8,11		
							70, ( $\pi_3^R$ )	2	1	97	8,13		
Compound VI							Compound VII						
80, ( $\pi_5^\beta-\sigma''^X$ )	35	65	0	5,94	7,66	1,72	80, ( $\pi_5^\beta-\sigma''^X$ )	35	65	0	6,00	7,74	1,74
79, ( $\pi_4^\beta-\sigma''^X$ )	39	54	7	6,88	8,65	1,77	79, ( $\pi_4^\beta-\sigma''^X$ )	40	57	3	6,97	8,74	1,77
78, ( $n_N$ )	3	97	0	7,22	9,14	1,92	78, ( $n_N$ )	3	97	0	7,28	9,06	1,78
77, ( $\pi_3^\beta+\sigma''^X$ )	20	69	11	7,54	9,30	1,76	77, ( $\pi_3^\beta-\sigma'^X$ )	38	44	18	7,59	9,32	1,71
76, ( $\sigma'^X$ )	71	22	7	7,62	9,52	1,90	76, ( $\pi_3^\beta-\sigma'^X+\pi_3^R$ )	37	38	25	7,67	9,48	1,81
75, ( $\pi_3^R-\sigma'^X$ )	25	13	62	7,85			75, ( $\pi_3^R-\sigma'^X$ )	26	11	63	7,74	9,63	1,89
74, ( $\pi_3^R$ )	0	0	100	8,04			74, ( $\pi_3^R$ )	14	10	76	8,00		

Figs. 4 and 5 display the photoelectron spectra of the vapor (thick line) of compounds **I-VII** fitted by Gaussian components (thin enveloping curve). In the spectra vertical lines correspond to the calculated electron energies shifted by the average Koopmans defect value. Dashed lines depict the nearest calculated electronic levels for which IEs were not determined.

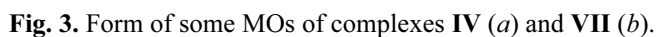
According to the results of the calculations, the first bands in the spectra of compounds **I-II** correspond to the  $b$  ( $\pi_3^\beta - \sigma'^X$ ) MO (Figs. 1 and 4). The second band in the spectrum of compound **I** is caused by photo ionization processes from three electronic levels. For compounds **I-II** the spectral region at 10 eV (Fig. 4) is due to the orbitals located mainly on

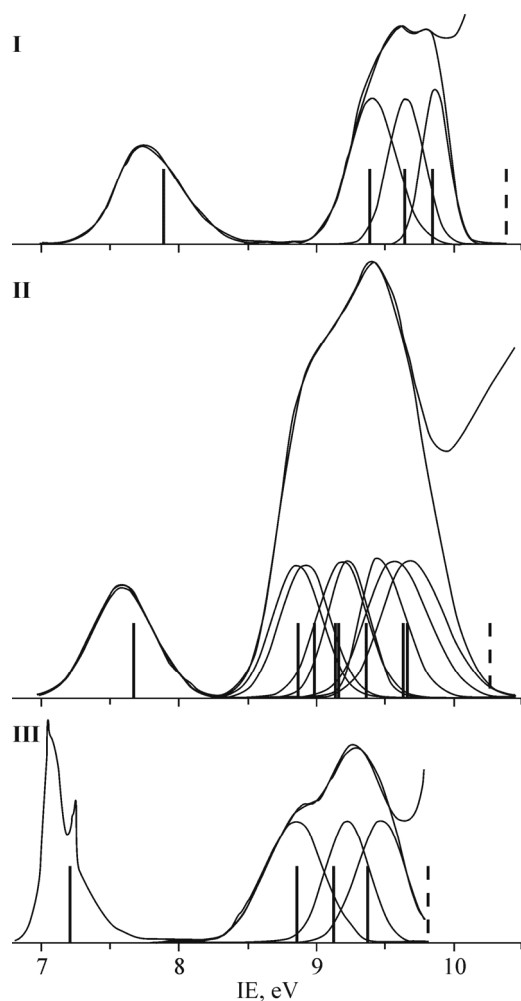


**Fig. 1.** Forms of three upper MOs of complexes **I** (a) and **III** (b).

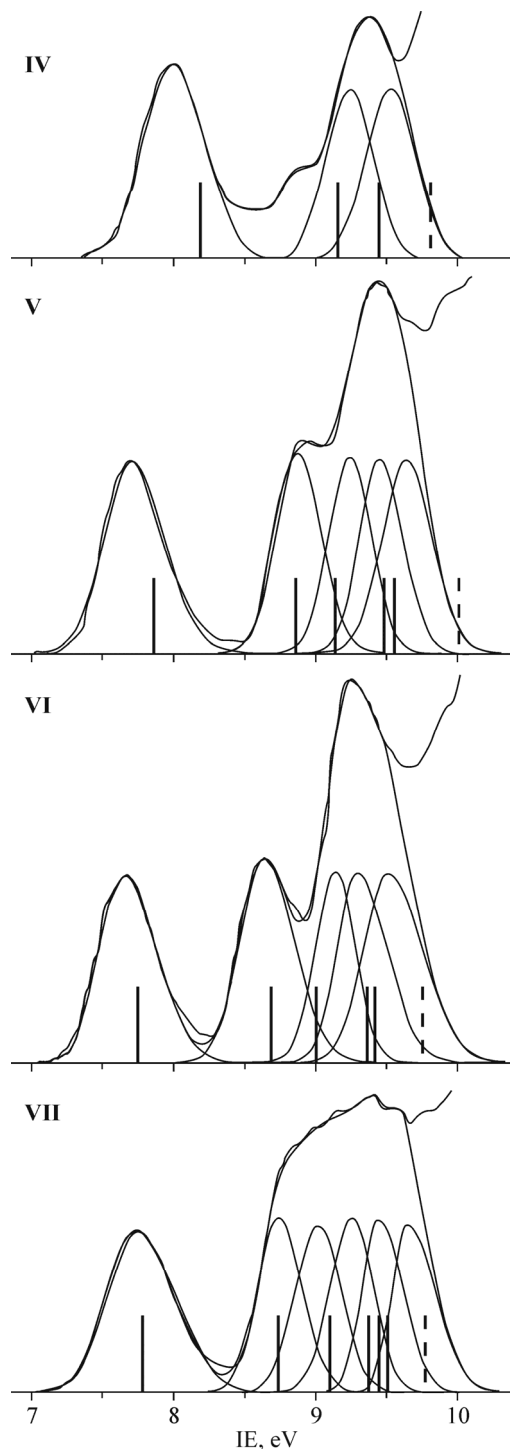


The occurrence of the vibrational structure in the first band of the UPS spectrum of compound **III** having the  $\pi$  system isoelectronic to that of the anthracene molecule is due to the C=C bonding  $\pi_7\beta$  MO located on three rings (Figs. 1 and 4). The second broad band is caused by ionization processes from three electronic levels (Fig. 4, Table 2). The spectral region at 10 eV (Fig. 4) corresponds to the  $\sigma^{\text{x}}$  MO.





**Fig. 4.** Photoelectron spectra of the vapor of compounds **I-III**.



**Fig. 5.** Photoelectron spectra of the vapor of compounds **IV-VII**.

In the spectra of complexes **IV-VII** the first bands are due to  $\pi_5\beta-\sigma''^X$  orbitals. They are followed by the bands corresponding to the number of MOs from one to five. The spectral region at 10 eV (Fig. 5) corresponds to the  $\pi_3^\beta + \sigma''^X$  orbital (complex **IV**) or MOs mainly located on substituents (compounds **V-VII**). The calculation shows that in the spectrum of compound **IV** the bend at 8.9 eV (Fig. 5) is caused by thermal destruction products of the sample.

For complexes **I**, **II**, and **III** the maximum distinction between the theoretical and experimental energies, with regard to the average Koopmans defects of 2.08 eV, 1.82 eV, and 1.96 eV, is 0.09 eV (Fig. 4, Table 2). In the series of compounds

**IV-VII** the average Koopmans defects  $\bar{\delta}_i$  (except the highest occupied MO) are 2.08 eV, 1.92 eV, 1.84 eV, and 1.79 eV respectively. The maximum discrepancy between the theoretical IEs ( $-\varepsilon_i + \bar{\delta}_i$ ) of the highest occupied MOs of compounds **IV-VII** and the maximum positions of the Gaussian bands reaches 0.18 eV (Fig. 5, Table 3). This can be explained by considerable rearrangement of the electron density (electron relaxation) when the electron is removed from HOMO. For the other upper occupied levels of complexes **IV-VII** the maximum distinction between experimental and theoretical IEs is 0.10 eV (Fig. 5, Table 3).

## CONCLUSIONS

For the complexes studied the noticeable mixing of the orbitals of the benzene and chelate rings, which is typical of boron  $\beta$ -diketonates, is absent [17, 23]. The interaction of the conjugated  $\pi$  systems of the five- and six-membered rings (compounds **V-VII**) results in the stabilization of the electron energies on the  $\pi_3^R$  MO.

The work was performed within the State Contract (No. 1137) of the Ministry of Education and Science of the Russian Federation and supported by the Scientific Foundation of the Far Eastern Federal University (grant 12-03-13008-16/13).

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