

PHOTOCHEMISTRY AND MAGNETOCHEMISTRY

Photoelectron Spectra and Electronic Structure of Boron Difluoride β -Diketonates with Aromatic Substituents

V. I. Vovna, S. A. Tikhonov, and I. B. Lvov

Far Eastern Federal University, Vladivostok, 690950 Russia

e-mail: lvov@vdo.dvgu.ru

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Abstract—The electronic structure of boron difluoride chelate complexes of the acetyl acetate type containing 4-biphenylene, 2-fluorene and 4-*trans*-stilbene as β -substituents is studied by means of photoelectron spectroscopy and quantum chemistry in the DFT approximation. It is established that the substituents affect the nature and sequence of the spectral bands. It is shown that calculation results corrected to the value of the Koopmans defect reproduce quite well the energy intervals between ionized states of complexes.

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

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INTRODUCTION

Boron difluoride chelate complexes have intense luminescence in a wide range of visible and near-infrared radiation [1–4], creating the possibility of their wide practical application. Expanding the fields of the practical use of this interesting class of the compounds requires that we study the regularities of excitation energy, ionization energy (IE) from the valence levels, and other characteristics of their electronic structure.

Earlier [5–8], we published the results from studies of the electronic structure of a series of β -diketonate complexes containing aromatic cycles on the carbonyl carbon atom by means of ultraviolet photoelectron spectroscopy (UVPES). However, interpreting the experimental IE only on the basis of spectral regularities hampers any clear determination of the nature and sequence of the electronic states. The current level of the development of quantum chemistry allows us to calculate the energy of the ionized states of molecules with a high degree of accuracy that serves as a reliable theoretical basis for the interpretation of experimental spectra.

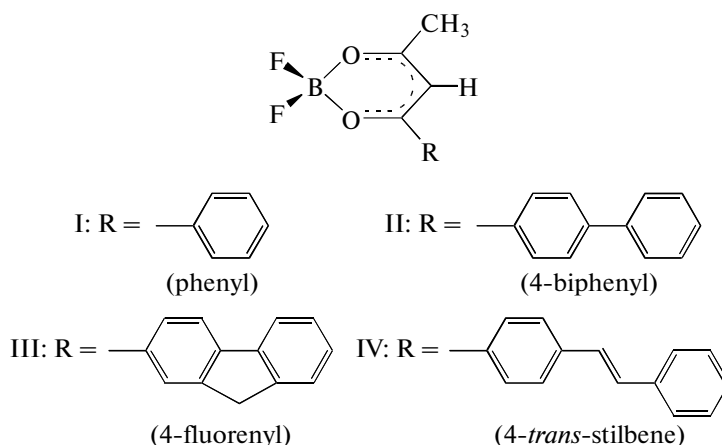
In [9], we used electronic density functional theory (DFT) to calculate the electronic levels and interpret the UVPE spectra of boron difluoride acetyl acetate F_2BAA and three complexes containing benzene cycles on the carbonyl carbon atom (C_6H_5 , *p*- $C_6H_4CH_3$, *m*- $C_6H_3(CH_3)_2$). Using the hybrid functional B3LYP5 and the relatively economical 6-311G basis for geometry optimization led us to the planar structure of boron difluoride benzoyl acetate F_2VBA . With good agreement between the experimen-

tal spectra and the calculated molecular orbitals (MOs), we established that the highest occupied molecular orbital (HOMO) is an antibonding combination of the highest π -orbitals chelate cycle and the phenyl radical $-C_6H_5$, and that introducing methyl groups into the substituent consistently reduces the contribution from the π_3 -orbital of the chelate cycle.

The Koopmans theorem, according to which the ionization energy of the molecule corresponding to the removal of the electron from the *i*th molecular orbital is the orbital energy ε_i taken with the opposite sign ($IE_i = -\varepsilon_i$), is widely used for interpreting photoelectron spectra. The ionization energy in the extended variant of the Koopmans theorem can be calculated with allowance for the Koopmans defect δ_i , an energy correction that is constant for a given MO type ($IE_i = -\varepsilon_i + \delta_i$). The δ_i value is a measure of the deviation of the calculated one-electron energies ε_i from the experimental values of the ionization energy and serves as a convenient instrument for analyzing photoelectron data [10].

Attributing the photoelectron spectrum bands to a Kohn–Sham MO in the approximation of the extended Koopmans theorem with allowance for the dependence of the Koopmans defect on the MO type led to good agreement between the theoretical results and the experiment as to the sequence and character of the electronic levels.

In this work, we present the results from studies of the electronic structure of boron difluoride complexes II–IV containing two benzene rings in the substituent R:



The effect of the polarization functions on the results from calculating the electronic structure was shown by the example of the F_2VBA compound (I) considered in [9].

CALCULATION METHODOLOGY

The calculations were performed using the Firefly 7.1.G quantum-chemical program [11]. The hybrid exchange–correlation functional B3LYP5 and the Ahlrichsa def2-TZVPP basis set [12–14] were used in DFT. Since the use of a more complicated def2-TZVPP basis instead of the 6-311G basis for calculating F_2VBA led to violation of the coplanar structure of the molecule, all further calculations were performed using the def2-TZVPP basis set. Earlier, we justified our choice of a basis set that includes the polarization functions for calculating the β -diketonate metal complexes from the example of zinc bis-acetyl acetonate [15]. Our calculations for $Zn(Acac)_2$ with the hybrid functional B3LYP5 in the Popple 6-31G*, 6-311G, Ahlrichsa def2-TZVPP, def2-QZVP, and Dunning cc-pVTZ basis sets [16] were performed in order to clarify the effect of the completeness of the basis on MO energy and composition. It was shown that after transitioning from the 6-311G basis set to def2-TZVPP, the geometric characteristics and total energies changes considerably. Further extension of the basis set leads to an increase in the computation time upon a slight change in the total energy and the geometric characteristics of the investigated systems.

Our choice of the functional was determined by test calculations for the acetyl acetonate metal complexes [9, 15]. A Hesse matrix was calculated to verify the correspondence of the optimized structures to the local minimum points on the potential energy surface for all compounds. The molecular orbitals were numbered in accordance with our calculations. In addition, the orbitals of each type were numbered according to their increasing energy. The UVPE spectra we published in [7, 8] were measured on an ES-3201 spectrometer with a He I radiation source, and

the accuracy of determining the maximum band positions was no less than 0.02 eV. The temperature of the ionization cuvette was as high as 200°C, depending on the vapor pressure.

RESULTS AND DISCUSSION

A comparison of the calculation results of complexes I–IV in the extended def2-TZVPP basis with the earlier results in the 6-311G basis reveals slight changes in MO energy and composition, but the coplanarity in the complex structure was notably violated. The dihedral angle between the planes of the benzene cycle and the two carbonyl bonds was 15° for F_2VBA (I), and the angle between the planes of the chelate cycle and the O–B–O fragment was 5°. The main reason for the geometric changes upon moving to a more complicated basis set was a better account of the interaction between the γ -hydrogen atom of the chelate cycle and the hydrogen atoms of aromatic rings. For compound I, the effect of basis extension on the MO energies and localization is demonstrated in Table 1. The change in orbital energy values ε_i after basis extension depends on the contribution from the π_3 -MO chelate cycle. The energy interval between the bonding and antibonding MOs grew from 0.76 to

Table 1. Orbital energies ($-\varepsilon_i$), energy difference ($\Delta\varepsilon_i$), and localization of the electronic density on the chelate cycle (ρ_c , %) and substituent R (ρ_R , %) for the four highest MOs of F_2VBA , calculated in the def2-TZVPP (numerator) and 6-311G bases (denominator)

MO	$-\varepsilon_i$, eV	$\Delta\varepsilon_i$, eV	ρ_c	ρ_R
54	7.22/7.40	0.18	68/67	32/33
53	7.69/7.77	0.08	0/0	100/100
52	8.03/8.16	0.13	41/49	59/51
51 (<i>n</i>)	8.79/8.88	0.09	92/94	8/6

Table 2. Localization of MO on substituent R (%); the energies of the Kohn–Sham orbitals; the positions of the band maxima, according to the results from the decomposition on Gaussians of the experimental spectrum (eV) and the parameter δ_i values (eV)

MO	Contribution R	$-\varepsilon_i$	IE_g	δ_i
Compound II				
74	81	6.74	8.81	2.07
73	46	7.41	9.48	2.07
72	86	7.41	9.49	2.08
71	95	7.69	9.77	2.08
70	81	8.28	10.35	2.07
69 (<i>n</i>)	8	8.73	11.00	2.27
Compound III				
77	84	6.49	8.29	1.80
76	94	7.22	9.19	1.97
75	33	7.38	9.33	1.95
74	92	7.56	9.55	1.99
73	84	8.39	10.31	1.92
72 (<i>n</i>)	8	8.66	10.76	2.10
Compound IV				
81	91	6.23	8.15	1.92
80	25	7.28	9.10	1.82
79	100	7.40	9.34	1.94
78	99	7.66	9.50	1.84
77	78	7.99	9.78	1.79
76 (<i>n</i>)	7	8.67	10.77	2.10
75	87	9.08	10.80	1.72

0.81 eV, which agrees better with the experimental value 0.88 eV (Table 2). Basis extension led to the reduction in electronic density transfer from the aromatic to the chelate cycle. The total charge of the

$-C_6H_5$ group, calculated in the approximation of the natural bonding orbitals (NBO) for I, was +0.11e in the 6-311 G basis and +0.07e in the def2-TZVPP basis.

The second bands with weak inflections in the spectra of compounds II–IV (Fig. 1) correspond to the ionization of three or four electronic levels. The decomposition of such bands into components in order to determine the energy and type of level without theoretical simulation of the ionized states is impossible.

To verify the quality of our reproduction of the IE values in the DFT approximation for lengthy π systems, we compared the known vertical ionization energy values IE_v [17] for biphenyl, fluorene and stilbene molecules with their calculated ε_i energies (Table 3). The value of the Koopmans defect (2.08 eV) was obtained by averaging the differences between the experimental and calculated energies for the 13 highest π -levels of biphenyl, fluorene, and stilbene. Only for MOs $4a_u$ and $2a_u$ of stilbene and the HOMO of fluorene did the deviations exceed 0.1 eV. Our method of calculation therefore reproduces quite well the energy intervals between the ionized states in the approximation we chose.

According to our calculation data for complex II, the dihedral angle between the planes of the chelate cycle and the benzene ring connected to the carbonyl carbon atom is close to zero, and the angle between the planes of two rings of the substituent is 38° . Analogous calculations for a free biphenyl molecule predicted a dihedral angle of 37° . In compound III, the boron atom lies in the plane of the chelate cycle; due to the effect of the methylene group, there is no violation of the coplanarity of the substituent's two cycles. In molecule IV, the second cycle of the substituent and the chelate cycle lie in one plane, but interaction with the hydrogen atom rotates the first cycle of the substituent by 2° – 3° . The dihedral angle between the plane of the chelate cycle and the O–B–O plane is 5° .

Figure 2 for compound II shows the shapes of four π -MOs that are of interest in interpreting the photoelectron and optical electronic spectra. The relative contributions from the substituents to II–IV are pre-

Table 3. Experimental and calculated IE for biphenyl, fluorene, and stilbene molecules (eV)

Biphenyl			Fluorene			Stilbene		
MO	IE_B	$-\varepsilon_i + 2.08$	MO	IE_B	$-\varepsilon_i + 2.08$	MO	IE_B	$-\varepsilon_i + 2.08$
$b_3(b_1^-)$	8.32	8.34	$3a_2$	7.92	8.04	$4a_u$	7.93	7.80
$a(a_2^-)$	9.05	9.10	$4b_1$	8.82	8.83	$3b_g$	9.13	9.13
$b_1(a_2^+)$	9.15	9.12	$2a_2$	9.12	9.05	$3a_u$	9.13	9.14
$b_2(b_1^+)$	9.80	9.71	$3b_1$	9.91	9.86	$2b_g$	9.42	9.42
$b_2(\sigma)$	11.20	11.20	$b_2(\sigma)$	11.00	11.10	$2a_u$	10.54	10.68

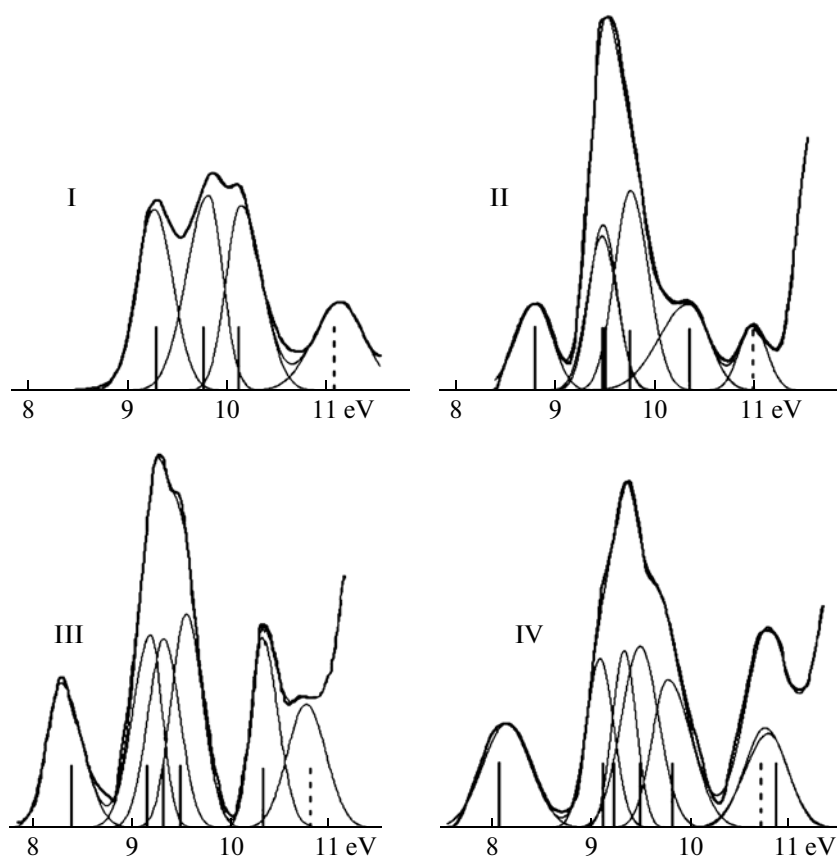


Fig. 1. UVPE spectra of compounds I –IV.

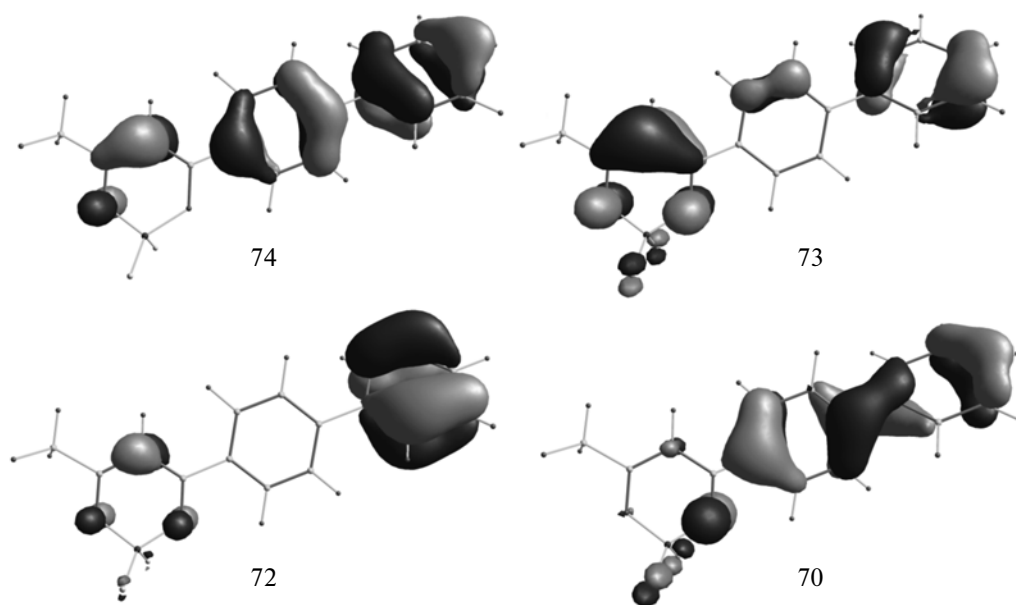


Fig. 2. Shapes of the four highest π -MOs of compound II.

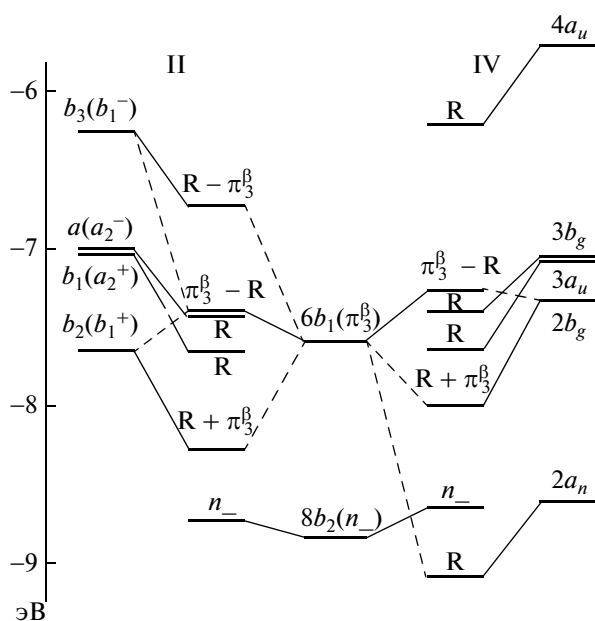


Fig. 3. Correlation of the π -orbitals of the biphenyl and stilbene molecules with the two highest MOs of F_2BAA for compounds II and IV.

sented in Table 2. The correlation diagram of the interaction between the MOs of the F_2BAA chelate cycle and the highest π -orbitals of the substituents was plotted according the calculation data for complexes II and IV (Fig. 3).

The acceptor chelate cycle in II stabilizes the MOs of the substituent by 0.4–0.7 eV while reducing the electronic density in the substituent cycles by 0.09e, along with the effect of the field caused by the positive charge of the carbonyl atom carbon. It is shown in Table 2 that in MOs 74 and 70 correlated with MOs $b_3(b_1^-)$ and $b_2(b_1^+)$ of biphenyl, the contribution from the π_3 -MOs of the chelate cycle (π_3^β) is estimated at 19%, and π_3^β -MOs make the greatest contribution (54%) to the 73rd electronic level. The orbitals 72 and 71 are almost completely localized on one of the rings of the substituent (see Fig. 2).

The energy interval between the π_3 and π_6 levels in the planar fluorene molecule with respect to biphenyl grows by 0.45 eV according to our calculation data, and by 0.50 eV according to the UVPEs data [17]. The energy intervals between the interacting levels in complex III larger than those in II reduced the mixing of π_3^β -MOs with the π -MOs of the substituent, but the dominant contributions to the five highest levels are similar (see Table 2). According to our calculation results, the intense second band in spectra of compounds II and III is due to the overlapping bands of

three states, one of which corresponds to the removal of the π_3 -electron of the chelate cycle.

The substituent in complex IV contains an additional pair of electrons of the bridging double bond in the π -system. It follows from the correlation diagram shown in Fig. 3 and the contribution from the fragments of complex IV (see Table 2) that the intense broad band in the UVPE spectrum of IV corresponds to four states. As in compound II, the π_3^β -orbital makes the main contribution to the second filled MO, 79 (75%), and less significant contributions to MOs 81, 77, and 75 (see Table 3). The bridging $\pi(C=C)$, in analogy with the stilbene molecule, makes close contributions to the highest (30%) and 75th (38%) MOs, localized mainly on the substituent. The n -MOs of the chelate cycle are located between the 75th and 77th π -orbitals.

The theoretically calculated number of electronic levels and the energy intervals between them were considered in decomposing the intense second bands in the spectra of compounds II–IV on Gaussians (see Fig. 1). In Table 2, the δ_i values as the IE differences for decomposition and the ε_i values are given for each level. The average δ value for π -electrons declines as the π system grows in the II–IV series. As we noted in [9], the δ values are 2.2–2.4 eV for n -orbitals in metal complexes $M(AA)_n$. When the calculated ε_i values were imposed on the spectra (see Fig. 1), the theoretical scale for each compound was corrected by the corresponding $\delta(\pi)$ value from Table 2, and the δ value for the n -orbital rises by 0.2 eV. Our analysis of the δ_i values for 16 levels of the π type in Table 2 showed that for only two levels (77 in III and 75 in IV) does the deviation from the average value exceed 0.1 eV, indicating good correlation of the intervals between the IE and the Kohn–Sham MO energies.

CONCLUSIONS

Note that unlike compounds with one benzene cycle on a carbonyl carbon atom, for which the interaction between the HOMOs of two cycles leads to close contributions from the π -orbitals to the bonding and antibonding MOs, the HOMOs in compounds II–IV are mainly localized on the substituent, and the chelate π_3^β -orbital makes the main contribution to the second or third MO.

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