

Photoelectron spectra and electronic structure of nitrogen analogues of boron β -diketonates



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ABSTRACT

The electronic structure of the valence levels of seven nitrogen-containing boron complexes was investigated using methods of ultraviolet photoelectron spectroscopy and density functional theory. The ionization energies of π - and σ -levels were obtained from photoelectron spectra. The electronic structure of nitrogen-containing compounds was compared with the electronic structure of β -diketonates. It was shown the influence of various substituents on carbon and nitrogen atoms of six-membered ring on the electronic structure of complexes. The changes in the electronic structure after the substitution of atoms in condensed cycles have been identified.

In order to compare the experimental vertical ionization energies IE_i with Kohn–Sham orbital energies ϵ_i we used the analogue of Koopmans theorem and average amendment to the orbital energy of the electrons (δ_i). For 26 electronic levels of seven studied complexes, the calculated values are in good accordance with experimental energy intervals between electron levels.

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1. Introduction

Boron β -diketonates ($X_2B(O-C(R_1)-C(R_2)-C(R_3)-O)$) possess an intensive luminescence [1–5] and are used because of these properties as laser dyes [6], active components of solar thermal collectors [7] and materials for electrophotography [8]. Due to the high biological activity of boron β -diketonates [9,10], they are also used as antiviral drugs.

The determination of relationships between the functional characteristics of substances and their electronic structure opens up opportunities for the direct synthesis of new compounds with prescribed properties. The electronic structure of boron β -diketonates has been studied using absorption [11–15] and photoelectron [16,17] spectroscopy. Earlier, we published the results of our studies of the electronic structure of boron β -diketonates based on the ultraviolet photoelectron spectroscopy (UPS) of vapours [18–20], X-ray electron spectroscopy of molecular crystals [18,20] and density functional theory (DFT) [18–20] methods.

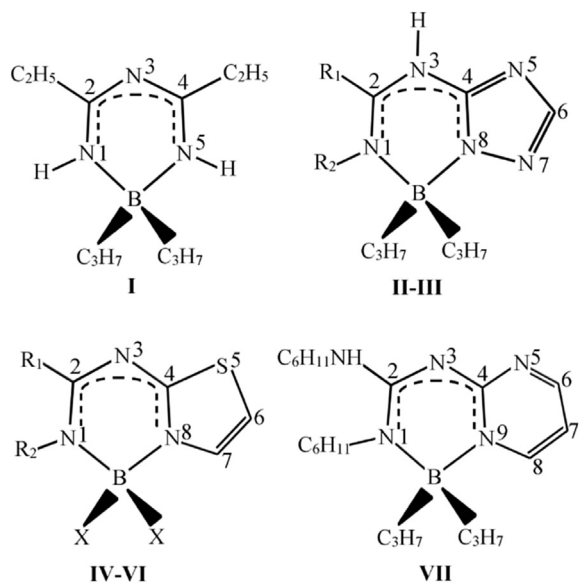
Nitrogen analogues of boron β -diketonates are also of scientific

and practical interest [21–23], but their electronic structure, unlike that of boron β -diketonates, has not been previously investigated by the UPS method.

This paper presents the results of a study of the electronic structure of seven nitrogen analogues of boron β -diketonates using UPS method and DFT approach. The usage of DFT for description of ionization states is based on an analogy between the Dyson's quasiparticle equation and Kohn–Sham equation. The general Dyson's equation [24,25] can be transformed to the Dyson's one-electron equation for the theoretical description of ionization processes [26]. The Kohn–Sham orbitals may serve as a good approximation to Dyson's orbitals in the case of valence ionization [27]. That's why Kohn–Sham Eigen functions are interpreted as approximate relaxed Dyson's orbitals, and respective Kohn–Sham orbital energies ϵ_i are interpreted as approximate relaxed ionization potentials [28–30]. The validity of this statement was checked on the example of several atoms and simple molecules [31–33]. Also in Refs. [18–20] it is shown that DFT allows the calculation of the energies of ionized boron complex states with a high accuracy, thus providing a good theoretical basis for the unambiguous interpretation of photoelectron (PE) spectra and analysis of valent electron levels of compounds I–VII.

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- II. $R_1 = R_2 = H$
 III. $R_1 = 4\text{-C}_6\text{H}_4\text{CH}_3$, $R_2 = H$
 IV. $X = \text{C}_4\text{H}_9$, $R_1 = R_2 = H$
 V. $X = \text{C}_4\text{H}_9$, $R_1 = 4\text{-C}_6\text{H}_4\text{CH}_3$, $R_2 = H$
 VI. $X = \text{C}_3\text{H}_7$, $R_1 = \text{C}_6\text{H}_{11}\text{NH}$, $R_2 = \text{C}_6\text{H}_{11}$

The spectra were interpreted, with use of dependence of the amendment to orbital energy on the nature of the molecular orbital [18–20]. The calculated parameters of the electronic structure of complex I have been compared with the data on the isoelectronic β -diketonate complex Ia.

2. Experimental and calculation methods

Samples were synthesized in the N. D. Zelinsky Institute of Organic Chemistry (Moscow) using methods described in Refs. [34–37]. The PE spectra of vapours of compounds I–VII were obtained on an ES-3201, converted electronic spectrometer with a He I ($h\nu = 21.2$ eV) monochromatic radiation source. The error in the determination of band maximums was within 0.02 eV. The ionization cuvette temperature depended on the vapour sublimation temperature of a particular sample and varied in the range of 180 °C to 220 °C. All spectra have bands with good resolution in the range of 6.5–10 eV. There is band overlap due to the high density of states in the range of energies above 10 eV.

In our DFT quantum chemistry calculations, we applied the Firefly 7.1.G software program [38] using the 6-311G (d) basic set [39]. The calculation results depend on type of exchange-correlation functional. At the present time the hybrid functionals [40], double-hybrid functionals [41], Minnesota functionals [42] and range-separated functionals [43,44] are used for DFT calculations. The method of dispersion correction as an add-on to standard Kohn–Sham density functional theory [45] is also used. In this paper, we study boron chelates built from H, B, C, N, and O atoms. The hybrid three-parameter functional [15,46–48] are successfully used for DFT calculations of boron complexes. The goal of our research is the electronic structure in ground state and the interpretation of ultraviolet photoelectron spectra. In our review [49] it was shown that hybrid B3LYP5 functional [50–52] gives good results for investigation of electronic structure of boron complexes by UPS method. Because we used B3LYP5 functional in our previous

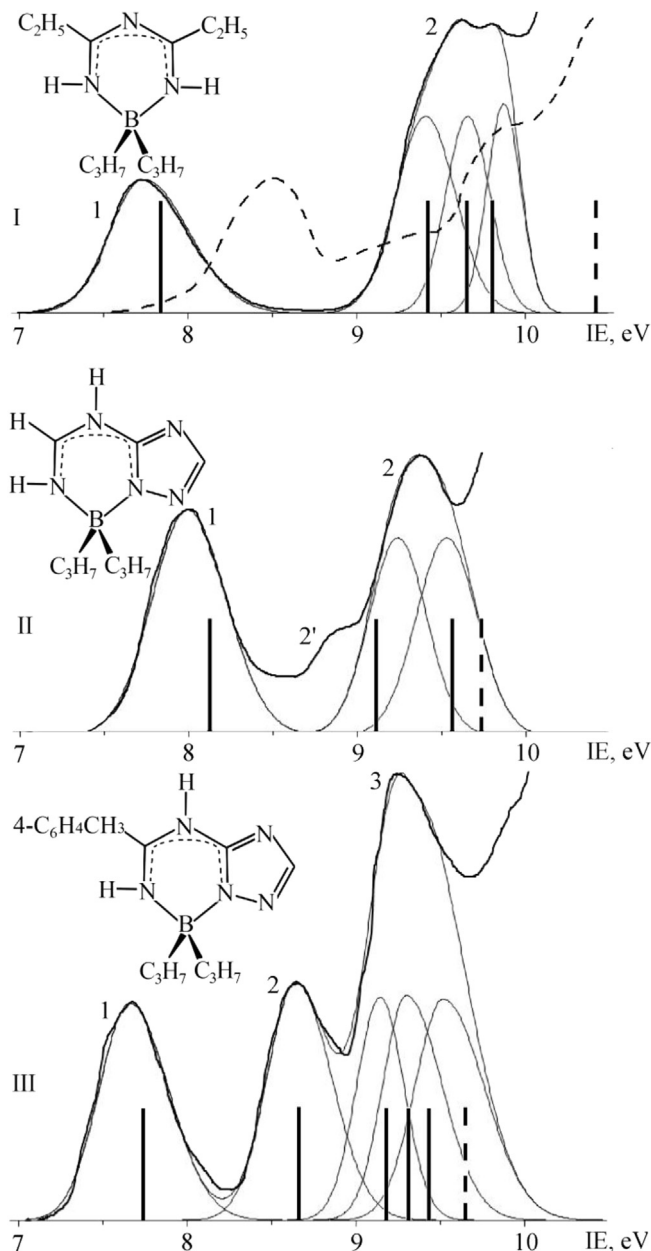


Fig. 1. Ultraviolet photoelectron spectra of the vapours of compounds I–III. The boron diethyl acetylacetonate spectrum [19] is indicated by a dotted line on the spectrum of compound I.

researches [18–20], we used it in this paper too. This allows excluding the influence of functional type on the electronic effects of substitution.

We calculated the Hessian matrix to check the correspondence between optimized structures and local minimum points on the potential energy surface. The absence of imaginary frequencies in the vibration spectrum indicated that minimum was reached on the surface of potential energy.

We used the analogue of Koopmans' theorem to compare the experimental values of vertical ionization energies (IE) with Kohn–Sham orbital energies ϵ_i :

$$\text{IE}_i = -\epsilon_i + \delta_i$$

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