



Electronic structure of binuclear acetylacetonates of boron difluoride

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The electronic structure of boron difluoride acetylacetonate and its three derivatives was studied using photoelectron and absorption spectroscopy, as well as the density functional theory. In a series of binuclear acetylacetonate complexes containing bridge-moieties of sulfur and selenium atoms, it was found an appreciable mixing of the π_3 -orbital of the chelate cycle with atomic orbitals S 3p and Se 4p resulting in destabilization of the HOMO levels by 0.4–0.6 eV, in comparison with the monomer. The positively charged fragment C(CH₃)-CX-C(CH₃) causes the field effect, which leads to stabilization of the LUMO levels by 0.3–0.4 eV and C 1s-levels by 0.5–1.2 eV. An analysis of the research results on the electronic structure made it possible to determine the effect of substituents in the γ position on the absorption spectra, which is mainly determined by the electron density transfer from the chalcogen atoms to the chelate cycles. It is shown that the calculated energy intervals between electron levels correlate well with the structure of the photoelectron spectra of valence and core electrons.

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1. Introduction

Derivatives of boron difluoride β -diketonates belong to a class of complexes that have been known for more than a century. These compounds possess a rich set of photophysical properties: intense luminescence in the entire visible and near-IR range [1–6], the ability to form excimers [7,8] and exciplexes [9,10], luminescent thermochromism [11], and liquid-crystalline polymorphism [12–15]. It is easy enough to obtain them by the Claisen condensation [16,17], that makes it possible to vary widely the structure and spectral characteristics. Boron difluoride β -diketonates show luminescence both in solutions and in the solid state, at that, these properties can differ significantly because they are associated not only with the molecular structure but also with various intermolecular interactions (hydrogen bonds, π - π -stacking interactions, short contacts, etc.). Therefore, the derivatives of boron difluoride β -diketonates are promising for a use as laser dyes [18], organic light-emitting diodes [19,20], optical chemosensors [21–23], active components of solar collectors [24], materials for nonlinear optics [25], and polymer optical materials [26,27].

Revealing relationships between the electronic structure and the spectral characteristics of boron difluoride β -diketonates opens opportunities for the controlled synthesis of new phosphors. The most reliable data on the electronic structure of chelates can be obtained by the joint using of methods of photoelectron spectroscopy and quantum chemistry. Direct measurement of the characteristics of individual levels by the methods of ultraviolet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS) [28] makes it possible to compare the obtained results with the theoretical electron energies.

There are many methods of quantum chemical modeling, but it is appropriate to calculate the ionization energies (IE) of molecules within the theory of molecular orbitals using the Kohn-Sham theorem [29] which was rigorously proved for the Hartree-Fock method. The application of its DFT analog [30] has shown that an average difference between the experimental and theoretical IEs in a series of 15 boron β -diketonates is 0.06 eV [31–33]. This is explained by the similarity of the Kohn-Sham equation (KS) and the quasi-particle Dyson equation for the valence electronic levels [34,35]. The general Dyson equation [36] is one of the ways to obtain the Green's functions [37]. A good correlation of the experimental data and the results of calculations in the approximation of the density functional theory (DFT) indicates on the reliability of the simulation results. A comparison of the absorption

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spectroscopy data and the results of calculations in the approximation of the time-dependent density functional theory (TDDFT) makes it possible to determine the influence of molecular structure on the optical properties of complexes.

Previously in Refs. [38–42], we investigated the relationship between the electronic structure and the optical properties of a number of classes of boron β -diketonates using the experimental methods XPS, absorption spectroscopy, and luminescent spectroscopy as well as DFT and TDDFT calculations. It is shown for the studied complexes that the results of DFT and TDDFT calculations correlate well with the experimental data of photoelectron and absorption spectroscopy. It makes it possible the unambiguous interpretation of UPS, XPS, and optical spectra as well as revealing the electronic effects of substitution. Unless [38–42], at present there are no experimental works on a profound study of relationships between the electronic structure and optical properties of boron difluoride β -diketonates.

The photophysical properties of boron chelates are determined by the nature of substituents in the β -positions (Scheme 1). The substitution in the γ -position is promising for formation of the complexes possessing chemical properties which are necessary for immobilization on the surface or for introduction into other structures. However, there is virtually no data on the substituent effect in the γ -position on the general properties of boron difluoride β -diketonates [43]. The binuclear acetylacetonates of boron difluoride are the simplest representatives of the class of

compounds in which the chelate cycles are rigidly located relative to each other because they are connected through a bridge in the γ -position that can lead to appearing of new photophysical properties. Thus, the synthesis and study of the electronic and molecular structure of these complexes is completely justified.

In this work, the results are presented on research of the electronic structure of boron difluoride acetylacetonate and its three derivatives (Scheme 1) using the data of photoelectron spectroscopy, absorption spectroscopy, and the data of DFT and TDDFT calculations.

2. Experimental and calculation methods

Compounds I–IV were obtained by the technique described in Ref. [44]. The absorption spectra were registered on a Helios α spectrometer in hexane solutions in cuvettes of 1 cm thickness (the solution concentrations were selected by diluting the saturated solutions).

Interpretation of the absorption spectra was performed on basis of TDDFT calculations of the singlet excited states. In order to include the excited states up to the vacuum ultraviolet energy (~ 8 eV), 50 electronic transitions were calculated for II–IV compounds. The calculated spectra were obtained from the values of the energies and oscillator forces (E_i , f_i) by summing the Gaussian curves $G_i(E) = a(f_i/d)\exp(-1/2(E-E_i)^2/d^2)$, where E is an energy, f is an oscillator strength, a is a factor to transform to the units of the molar extinction coefficient, i is a number of transition, d is a half-width parameter. The solvent effect was taken into account with the dielectric permittivity of hexane within the continuum solvation model SMD.

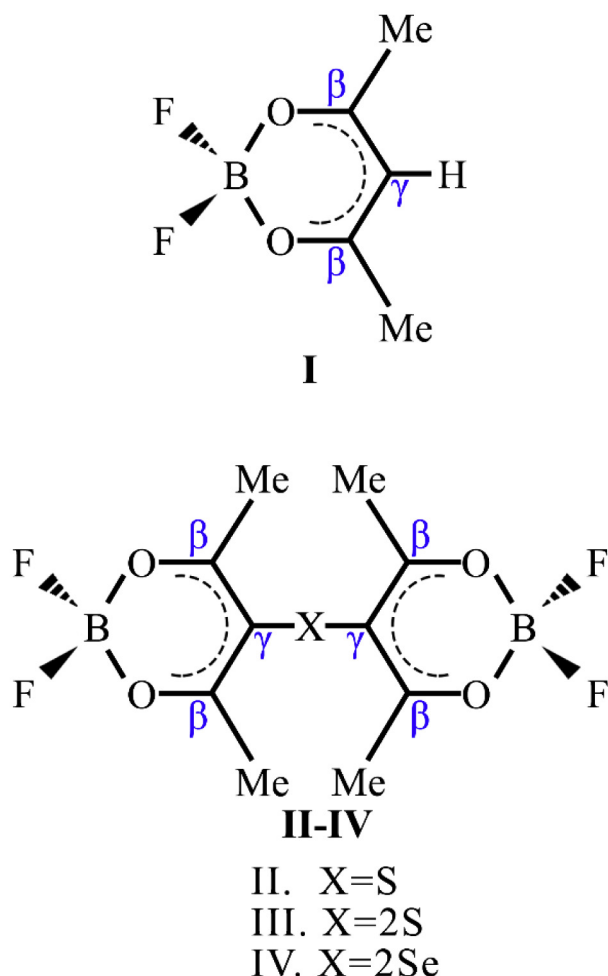
The UPS spectrum of vapors of the compound I was obtained on a modified ES-3201 electronic spectrometer with a hemispherical electrostatic analyzer and a monochromatic light source He I ($h\nu = 21.2$ eV). In order to calibrate the spectrum the inert gas Xe was introduced simultaneously with the substance into the chamber. The error in determining the band maxima did not exceed 0.04 eV. The temperature of the ionization cuvette was 220 °C. The UPS spectrum of the complex I possesses the defined bands in the energy range from 9 to 16 eV.

In order to compare the experimental bands of the UPS spectrum of the compound I with the orbital energies KS ε_i it was applied a procedure being similar to the extended Koopman's theorem:

$$|E_i| = -\varepsilon_i + \delta_i,$$

where $|E_i|$ is the ionization energy; ε_i is the single-electron energy KS; δ_i is a defect of the DFT approximation (DFA-defect) that is a measure of deviation of the calculated single-electron energies ε_i from the experimental vertical $|E_i|$.

XPS spectra of molecular crystals of the compounds II–IV were obtained on a high-vacuum photoelectron spectrometer (Omicron, Germany) with a hemispherical electrostatic analyzer. The photon energy was 1253.6 eV (MgK α). The instrumental function of the spectrometer in a recording mode of the characteristic levels of atoms, determined by a contour of the Ag3d $_{5/2}$ band, had a half-width of 1.2 eV. The calibration of the electron binding energy scale (E_b) over the F 1s (686.0 eV) levels was performed using the internal standard technique, which was successfully applied in Refs. [41,45]. At determining the atomic concentrations of elements in a sample, the relative cross sections of ionization and the depth of photoelectron escape were taken into account. The relative concentration of elements, obtained from the band intensities of 1s-electron, coincided with the calculated values within the method error (10%).



Scheme 1. Chemical structure of the studied complexes.

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