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Electronic structure and optical properties of boron difluoride naphthaloyl- and anthracenoylacetonates

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ABSTRACT

Electronic structure and optical properties of boron difluoride naphthaloyl- (I) and anthracenoylacetonates (II) have been studied by the methods of photoelectron, absorption, luminescence spectroscopy as well as by quantum chemistry (DFT and TDDFT). In contrast with compound (I), the correlation of energies and types of transitions in excited states between compound (II) and anthracene molecule are ascertained. In addition, the bathochromic shift of the luminescence band maximum and decrease of luminescence quantum yield are detected. The decrease of luminescence quantum yield correlates with the reduction of C-C bond order between chelate ring and substituting group and with the decrease of the excited state lifetime. The good agreement between UV/X-ray photoelectron spectra data and Kohn-Sham orbital energies and structure confirms the reliability of the results of quantum-chemical modeling.

1. Introduction

Boron difluoride β-diketonates have intensive luminescence in the visible and near-IR range [1–6], ability to form excimers [7,8] and exciplexes [9,10], luminescence thermochromism [11] and liquid-crystal polymorphism [12–15]. These compounds are used as laser dyes [16], organic light-emitting diodes [17,18], optical chemosensors [19–21], active components of sunlight collectors [22], materials for non-linear optics [23] and polymer optical materials [24,25]. The investigation of the electronic structure of boron difluoride β-diketonates and their spectral properties opens the possibility for direct synthesis of new luminescent material. The most reliable information on the electronic structure of chelates can be obtained by joint application of methods of ultraviolet photoelectron spectroscopy (UPS), X-ray photoelectron spectroscopy (XPS) and quantum chemistry. Comparison of ionization energies obtained from photoelectron spectra [26], with the energies of Kohn-Sham (KS) molecular orbitals, makes it possible to reveal the features of the electronic structure of the systems under study.

A good correlation of the experimental and theoretical ionization energies indicates the reliability of the results of quantum-chemical modeling. The usage of the methods of absorption and luminescent spectroscopy in conjunction with the results of calculations in the approximation of the nonstationary density functional theory (TDDFT) makes it possible to establish relationships between the molecular design and the optical properties of boron difluoride complexes on the basis of analysis of substitution effects.

In [27–31], we showed that the results of calculations of the electronic structure of boron β-diketonate complexes in the DFT and TDDFT approximations correlate well with the experimental results obtained by photoelectron and optical spectroscopy. This makes it possible to exactly interpret photoelectron and optical spectra, as well as to analyze electronic substitution effects.

Earlier [27,28], we investigated the electronic structure and optical properties of boron difluoride dibenzoylmethanate and its four derivatives using XPS, absorption spectroscopy, luminescent spectroscopy, and DFT/TDDFT calculations. At present, there are no other publications devoted to a detailed study of the electronic structure of boron difluoride β-diketonates, which determines their luminescent properties.

The interest in the research of naphthaloyl (I) and anthracenoylacetonates (II) of boron difluoride is determined by their luminescent properties [32] and the prospect of creating new functional materials for phase holograms and integrated optical elements [33].

In this paper, we present the results of an investigation of the electronic structure and optical properties of compounds I-II (Scheme 1)

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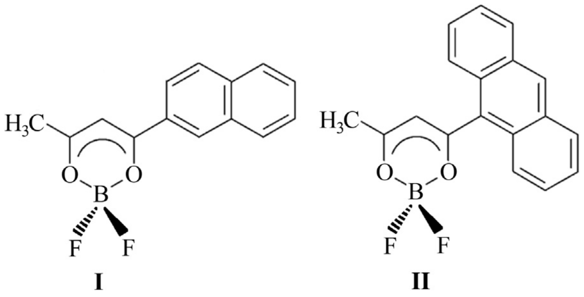

Scheme 1. Chemical structure of compounds I and II.

according to the methods of UPS, XPS, absorption spectroscopy, luminescence spectroscopy, and the results of calculations in the DFT and TDDFT approximations.

2. Experimental and calculation methods

Compounds I and II were prepared and purified according to [8,32] correspondingly. The absorption spectra were registered using a Shimadzu-UV2550 spectrometer (Japan). Anthracene solution used as a standard for measuring the fluorescence quantum yield ($\varphi_F = 0.27$) [34]. The measurements of fluorescence lifetime by time-correlated single-photon counting (TCSPC) were performed using a FluoTime 200 device (PicoQuant, Germany) with a LDH-P-C-375 (370 nm) excitation source and a TimeHarp device as the SPC controller. The lifetime data were analyzed using the FluorFit 4.0 software from PicoQuant. Chloroform was purchased from Roshimreaktiv and used as received.

UPS spectra of compounds I and II in a vapor phase were obtained on a modified electronic spectrometer ES-3201 with hemispherical electrostatic analyzer using monochromatic irradiation source He I ($h\nu = 21.2$ eV). To calibrate spectra, xenon was used. The error in determining the band maxima did not exceed 0.02 eV. The temperature of the ionization cuvette depended on the sublimation temperature of the vapor and was in the range from 200 to 240 °C.

To compare the experimental values of vertical ionization energies (IE) with KS orbital energies ε_i we used a procedure similar to the extended Koopmans' theorem:

$IE_i = \varepsilon_i + \delta_i$,

where

IE_i — ionization energy;
ε_i — single-electron KS-energy;
δ_i — defect of density functional theory approximation (DFA-defect), which reflects the deviation of calculated single-electron energy ε_i from experimental vertical IE_i.

XPS spectra of molecular crystals of I and II were recorded by using a high-vacuum photoelectron spectrometer (Omicron, Germany) with a hemispherical electrostatic analyzer using a monochromatic radiation source MgKα ($h\nu = 1253.6$ eV). The apparatus function of the spectrometer in the mode of recording of the characteristic levels of atoms, determined from the contour of the Ag $3d_{5/2}$ band, had a width at half-height of 1.2 eV. The calibration of the electron binding energy scale (E_b) is performed by the internal standard technique, which is the level of F 1 s (686.0 eV). When determining the atomic concentration of elements in the sample, the relative ionization cross sections and the photoelectron escape depth were taken into account. The relative concentrations of elements, obtained from the band intensities of 1s-electron, coincided with the calculated values by taking into account the method error (10%).

The bands of the XPS spectra of the valence and core levels are interpreted taking into account the number of calculated electronic levels, the energy intervals between them and the relative ionization cross sections.

The calculation method was chosen based on a good correlation between the experimental and theoretical ionization energies [31]. This is explained by the similarity of the Kohn-Shem equation and the Dyson quasiparticle equation. It was shown in [35,36], that in the valence region the KS orbitals can act as a good approximation to the Dyson orbitals. The general Dyson equation [37] is one of the methods for obtaining the Green's functions [38]. DFT and TDDFT calculations were performed using Firefly 8.1.G [39] and TZVP basic set [40,41]. The calculation results depend on the type of exchange-correlation functional. Now the hybrid [42], double-hybrid [43], Minnesota [44] and range-separated functionals [45,46] are used for DFT calculations. The method of dispersion correction as an add-on to standard KS density functional theory [47] is also used. The hybrid three-parameter B3LYP functional is successfully used for DFT calculations of boron complexes [48–54]. In our review [31] it was shown that hybrid B3LYP functional [55–57] gives good results for investigation of the electronic structure of boron complexes by UPS and XPS methods. Therefore, in this paper all calculations were performed using the B3LYP functional.

To interpret the optical spectra, the results of TDDFT calculations were used. To cover excited states up to vacuum ultraviolet energies (~8 eV), 50 electronic transitions for compounds I-II, naphthalene and anthracene were calculated. The calculated spectra are obtained from the values of the energies (E_i) and oscillator strengths (f_i) by summing the Gaussian curves $G_i(E) = a(f_i/d)\exp(-{}^1/_2(E-E_i)^2/d^2)$, where a is a factor to transform to the units of the molar extinction coefficient; i is the sequence number of the transition; d is the half-width parameter.

3. Results and discussion

3.1. Modeling of electronic structure

Optimization of the geometric parameters of I and II resulted in a slight (the few degrees) break in the plane of the chelate ring along the O-O line. For compound I, the violation of the coplanarity of the planes of the chelate ring and the substituent is 7°. In complex II, due to repulsion between hydrogen atoms in the γ-position of the chelate ring and at positions 1 and 8 of the anthracene fragment, the dihedral angle between the planes of the aromatic substituent and the chelate ring is 57°.

Fig. 1 shows the shapes of some molecular orbitals of compounds I and II. Table 1 shows the calculated molecular level energies ($-\varepsilon_i$) and the experimental ionization energies (IE_i) of compounds I and II according to the UPS method. The types of KS highest occupied molecular orbitals (MO) are determined from the contributions of Mulliken atomic populations, and for vacant MOs by the relative sum of the squares of the coefficients of the basic orbitals. π-Orbitals are conventionally divided into localized mainly on: chelate ring *a* (F_2B-O-C-CH-C-O-) and substituents *b* (naphthyl, anthryl). The delocalized MOs are conditionally designated as "*ab*" or "*ba*", depending on the prevailing localization. Orbitals *a* and *b* are considered mixed if the sum of the Mulliken atomic populations for each of the fragments is greater than 20%.

In order to interpret the ultraviolet and X-ray photoelectron spectra of compounds I and II, the structure of the valence and core levels was analyzed. To demonstrate electronic substitution effects, Fig. 2 shows a correlation diagram of the calculated levels of compounds I and II, naphthalene, anthracene and boron difluoride acetylacetonate (BF_2Acac). In compound I, the highest occupied molecular orbital (HOMO) is localized predominantly on a substituent (Table 1, Figs. 1 and 2b). Next are the antibonding and bonding combinations of the π_4-orbitals of the naphthyl group and π_3 of the chelate ring, as well as the π_3 and n-MOs of chelate rings (Fig. 2). In compounds I and II, the chelate ring stabilizes the orbitals of the substituents by 0.2–0.6 eV (Fig. 2) due to both the decrease in the electron density in the substituents (0.08e for I, 0.04e for II) and the field effect caused by the positive charge of the carbonyl carbon atom.

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