02

Luminescence of boron difluoride ditoluoylmethanate. Formation of J-aggregatess

© A.G. Mirochnik, E.V. Fedorenko, A.Yu. Beloliptsev

Institute of Chemistry of the Far-Eastern Branch of the Russian Academy of Science,
690022 Vladivostok, Russia

e-mail: gev@ich.dvo.ru

Received on May 27, 2021
Revised on August 21, 2021
Accepted on September 06, 2021

The processes of the formation of J-aggregates during the dissolution 2,2-difluoro-4,6-di(4′-methylphenyl)-1,3,2-dioxaborine crystals (**1**) and their subsequent dissociation have been studied by absorption and luminescence spectroscopy and quantum-chemical modeling. It is shown that two luminescent centers are observed in the solution **1**: monomeric luminescence and luminescence of J-aggregates (dual luminescence). Evolution of absorption, excitation and luminescence spectra is observed over time, indicating a slow dissociation of J-aggregates.

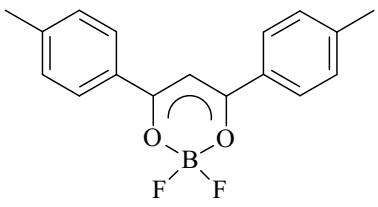
Keywords: luminescence, absorption spectra, boron difluoride complexes, J-aggregates.

DOI: 10.21883/EOS.2022.02.53212.1717-21

Introduction

Boron difluoride β-diketonates — are highly luminescent, highly polar compounds capable of self-organization: excimer formation [1,2], gel formation [3,4], formation of photostable excimers jcite5 and exciplexes [6] in polymer matrices. The self-organization ability determines the properties such as mechanochromism, thermochromism [7,8], size-dependent luminescence [9]. In this connection, aggregates formation by molecules of boron difluoride β-diketonates in solutions and polymer matrices and formation of new luminescent centers based on them are of interest.

As a rule [10,11], absorption bands of aggregates are not observed, but the luminescence excitation spectrum contains an intense long-wavelength band corresponding to excitation of loosely bound aggregates, similar to those described by Weber [12]. Earlier [13] we managed to find a compound , 2,2-difluoro-4-methylnaphtho-[2,1-e]- 1,3,2-dioxaborine, for which J-aggregates are registered in the absorption spectra. This is due to the fact that the molecule is rigid (consists of two condensed aromatic rings and a quasi-aromatic chelate ring) and does not have bulky groups (or substituents). In this report, we present one more rare example (for boron difluoride β-diketonates) that makes it possible to observe J-aggregates formation in solution: 2,2-difluoro-4,6-di(4′-methylphenyl)-1,3,2-dioxaborine (**1**) (diagram).



Scheme.

Experimental part

Solutions were prepared using EKOS-1 chloroform without preliminary purification. 2,2-Difluoro-4,6-di(4′-methylphenyl)-1,3,2-dioxaborine was obtained and purified according to the procedure given in [14].

Absorption spectra were recorded on a Shimadzu UV-2550 spectrometer. Luminescence excitation and luminescence spectra were recorded on a Shimadzu-RF5301 spectrofluorimeter in 10×10mm cells. When studying the luminescence spectrum dependence on the exciting light wavelength and the luminescence excitation spectra on the wavelength of concentrated solutions luminescence recording, to eliminate the effect of the internal filter, the spectra were recorded with the 10×1 mm cell in the front position.

Model quantum-chemical calculations of a single molecule and dimers of boron difluoride ditoluylmethanate were carried out using the Gamess [15] software package by the BHF SCF (bounded Hartree–Fock self-consistent field) method in the basis 6-311G(p,d) with addition of the B3LIP density functionality in experimental geometry. The molecule geometry is fully optimized. The solvent effect was taken into account using a polarizable continuum model (PCM).

Results and discussion

To record absorption spectra **1**, a chloroform solution was prepared with concentration of $C = 5 \cdot 10^{-6}$ mol $\cdot$ L^{-1}; the solution was prepared by serial dilution from the solution with $C = 1 \cdot 10^{-3}$ mol $\cdot$ L^{-1}. The optical density of the solution is 0.018, which, seemingly, makes it possible to consider the solution as dilute and ignore intermolecular interactions. In the absorption spectrum, similarly to

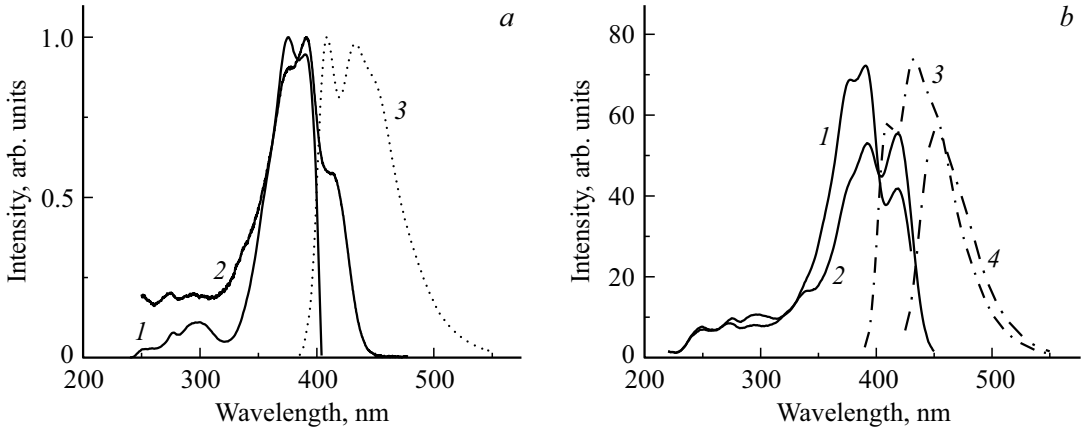


Figure 1. (*a*) Normalized absorption spectra of **1** solution in chloroform: *1* — $C = 1 \cdot 10^{-6}$ mol · L^{-1}, *2* — $C = 5 \cdot 10^{-6}$ mol · L^{-1}; *3* — luminescence spectrum of a solution with $C = 1 \cdot 10^{-6}$ mol · L^{-1}. (*b*) Solution spectra **1** in chloroform with $C = 5 \cdot 10^{-6}$ mol · L^{-1}: excitation: *1* — $\lambda_{reg} = 440$ nm, *2* — $\lambda_{reg} = 470$ nm; luminescence: *3* — $\lambda_{ex} = 380$ nm, *4* — $\lambda_{ex} = 417$ nm.

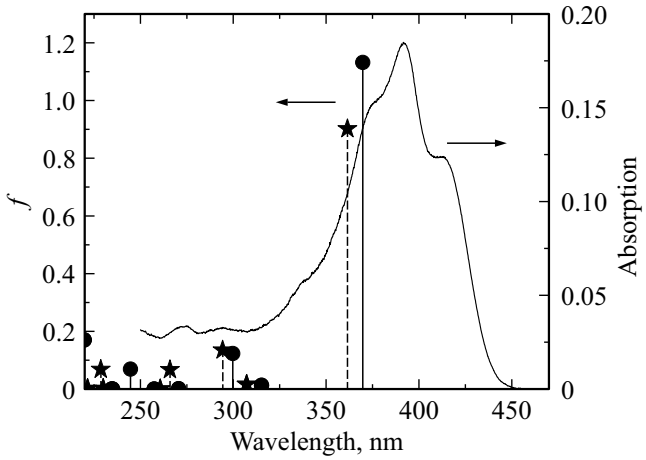


Figure 2. Absorption spectra of a **1** solution in chloroform: experimental $C = 5 \cdot 10^{-6}$ mol · L^{-1} (*1*), calculated for experimental geometry (asterisks), calculated for optimized geometry (circles).

the boron difluoride dibenzoylmethanate spectrum [10], an intense band with a pronounced vibrational structure (377, 393 nm, Fig. 1, *a*) is observed. In addition, the spectrum contains an arm of 412 nm, which is not typical for boron difluoride β-diketonates [11,16] and is absent in the theoretical spectrum (Fig. 1, 2). As the solution concentration decreases to 10^{-6} mol · L^{-1}, the 412 nm band disappears, which allows us to attribute it to absorption of intermolecular aggregates (J- aggregates).

In the monomeric luminescence spectrum **1** (10^{-6} mol · L^{-1}), as well as in the absorption spectrum, a vibrational structure is observed (Fig. 1, *a*), the excitation spectrum corresponds to the absorption spectrum. As the solution concentration increases to $5 \cdot 10^{-6}$ mol · L^{-1}, 422 nm band appears in the luminescence excitation spectrum, corresponding to the absorption band of 412 nm. In this case, dual luminescence appears: when the detection wavelength changes from 440 to 470 nm, the aggregates excitation band increases significantly in the excitation spectrum (Fig. 1, *b*). The luminescence spectrum recorded at $\lambda_{ex} = 415$ nm (aggregate absorption wavelength) is bathochromically shifted relative to the spectrum recorded at $\lambda_{ex} = 380$ nm (monomer excitation wavelength) (Fig. 1, *b*). Thus, two luminescent centers are observed in solutions **1**: monomeric luminescence ($\lambda_{ex} = 380$ nm, $\lambda_{lum} = 407$ and 430 nm) and J-aggregate luminescence ($\lambda_{ex} = 420$ nm, $\lambda_{lum} = 450$ nm).

The presence of two luminescence centers in solutions **1** (monomeric and J-aggregates luminescence) is confirmed by the different nature of the concentration dependence of the luminescence intensity on the exciting light wavelength (Fig. 3, 4). The dependence of the concentration quenching efficiency on the exciting light wavelength is described in [17] and explained by formation of intermolecular

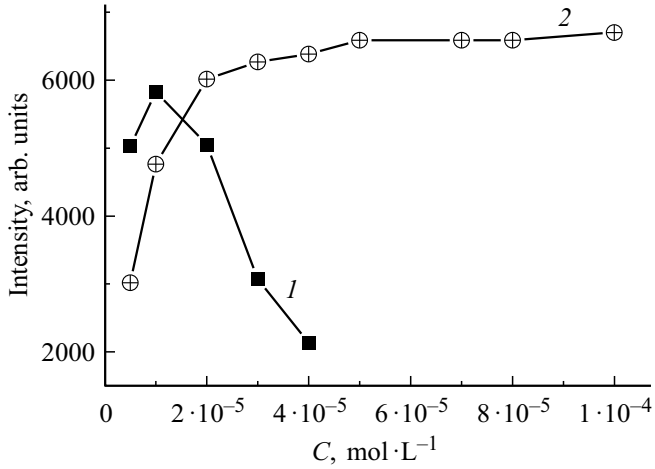


Figure 3. Dependence of the integrated intensity of the freshly prepared solution luminescence **1** on the luminophore concentration at different wavelengths of the exciting light: *1* — $\lambda_{ex} = 380$ nm; *2* — $\lambda_{ex} = 430$ nm.

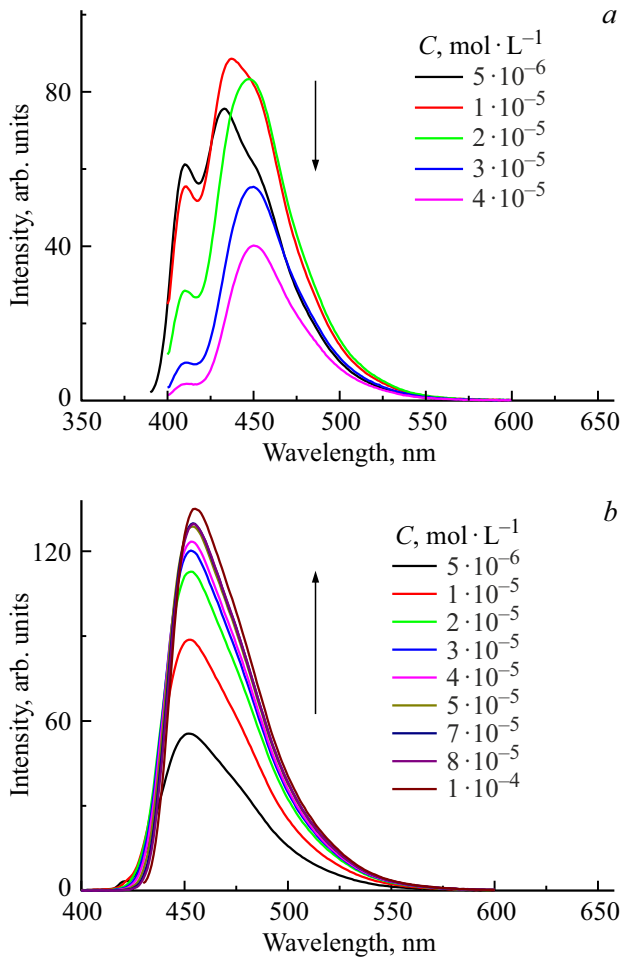


Figure 4. Luminescence spectra of solutions **1** in chloroform: (a) — $\lambda_{ex} = 380$ nm; (b) — $\lambda_{ex} = 430$ nm.

aggregates excited by a wavelength other than the maximum of the absorption spectrum of single molecules.

When solutions **1** are stored in chloroform for two days, pale yellow solutions discoloration and a hypsochromic shift of the luminescence spectra is observed (Fig. 5). Change in the spectral characteristics is not associated with the chemical decomposition of luminophore: the data of TLC (thin layer chromatography) comparison and IR spectroscopy of substances in freshly prepared solution and in solution standing for two days solutions are identical.

In the absorption spectrum of the discolored solution, the J-aggregates absorption band disappears (Fig. 5, a), and a hypsochromic shift of the absorption spectrum maximum occurs. The luminescence and luminescence excitation spectra also shift to the blue region and for solutions with concentration of $5 \cdot 10^{-6}$ and 10^{-5} mol · L^{-1} coincide with the monomeric luminescence spectra of the solution with $C = 10^{-6}$ mol · L^{-1} (Fig. 1, a and 5, b). The observed evolution of the spectra indicates dissociation of J-aggregates in dilute solutions **1** over time.

Slow dissociation **1** is due to the features of its crystal structure. The crystal structure **1** was determined in the article [14]. The CIF file has been deposited with the CCDC with number 23428. Despite the presence of identical substituents (methyl groups) in both phenyl rings in the *para*-position, the **1** molecule in the crystal is asymmetric [13]. As a rule, a slight distortion of the molecule occurs due to the achievement of the closest packing in the crystal [18]. Molecules **1** in a crystal are organized into skewed stacks (Fig. 6, a) [13]. The following short contacts are identified in the **1** structure: between the hydrogen atoms of the methyl groups and the aromatic rings of neighboring molecules (Fig. 6, a); between the hydrogen atoms of the phenyl rings and the fluorine atoms of the neighboring molecule (Fig. 6, b). In a stack, this corresponds to π-stacking and C−H...π-stacking interactions. The stacks are interconnected by a weak C−H...F hydrogen bond, which is characteristic of boron difluoride β-diketonates and plays an important role in their molecules self-organization [19]. Molecule rows linked by C−H...F bonds form layers (Fig. 6, b).

Total energies (E_{tot}) of monomer and dimers **1** calculated by the PCM method and energies of dimers formation (ΔE_{form})

	E_{tot}, at.units	ΔE_{form}, at.units
Monomer	−1031.45725	
Dimer „head−head“	−2062.9142	−0.0003
Dimer „head−tail“	−2062.9174	−0.0030

The luminescent properties of crystals **1** (λ_{ex}=485 nm, λ_{lum} = 520 nm) are due to formation of J-aggregates in the structure of the crystal and excimers based on them [14]. In turn, J-aggregates consist of dimers, which are excimer traps (Fig. 6, a).

Usually, the energy required to separate a molecule from the crystal and the solvation energy of the separated molecule are taken into account during crystal dissolution. For **1**, interactions in the stack (dimer „head−head“) and in the layer (dimer „head−tail“) were estimated using quantum chemical simulation (Fig. 7). Total energy for dimers was calculated by the PCM method for the experimental geometry. The dimer „head−tail“ (table) is more favorable due to ormation of the C−H...F hydrogen bond (Fig. 6b). The destruction energy of the dimer „head−head“ is an order of magnitude lower than that of the dimer „head−tail“ (Table). Correspondingly, when a crystal is dissolved, stack structures are first destroyed and supramolecular band structures are formed, in which **1** molecules are connected by C−H...F-bonds. It is the band structure of **1** aggregates in solution that explains the absence of excimer luminescence, in contrast to (520 nm) [13] crystals.

For the **1** molecule, according to the calculation data, the optimal structure is a structure with a symmetry plane along the boron atom line — central carbon atom of the chelate cycle. The value of the total energy of the **1** molecule

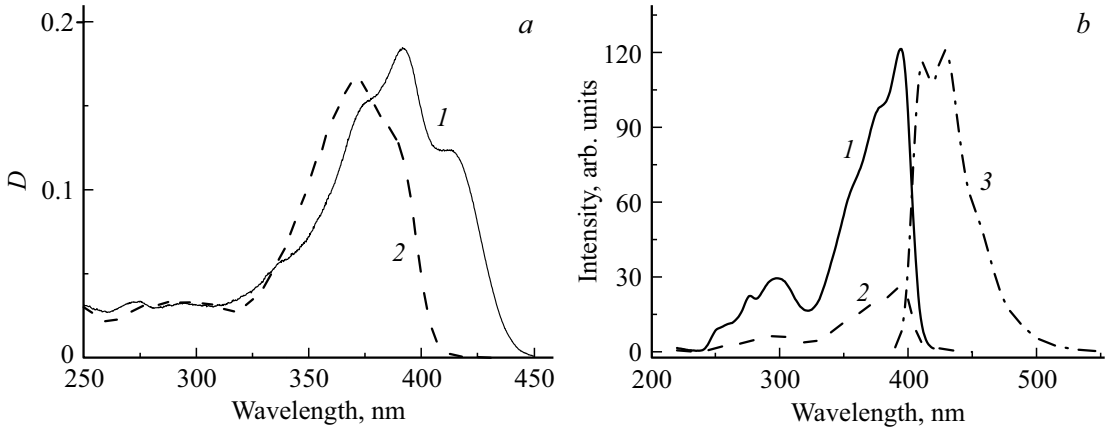


Figure 5. (*a*) Absorption spectra of the solution **1** in chloroform $C = 5 \cdot 10^{-6}$ mol · L^{-1}: *1* — freshly prepared, *2* — two days after preparation; (*b*) excitation spectra of the solution **1** in chloroform with $C = 5 \cdot 10^{-6}$ mol · L^{-1} two days after preparation: *1* — $\lambda_{reg} = 430$ nm, *2* — $\lambda_{reg} = 470$ nm; *3* — luminescence spectrum, $\lambda_{ex} = 380$ nm.

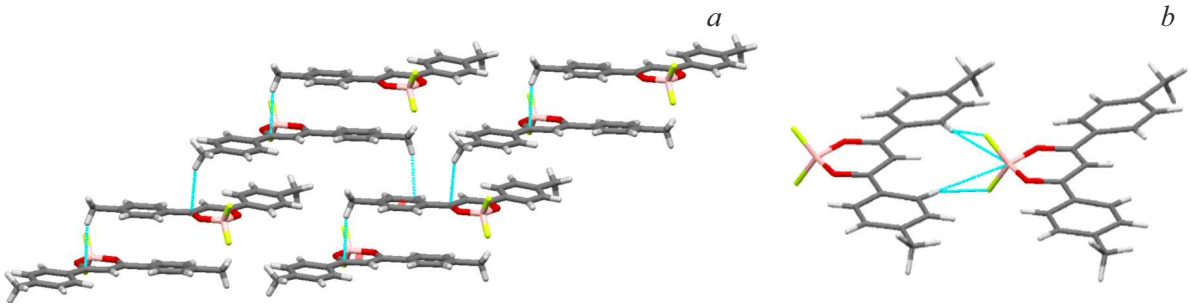


Figure 6. Intermolecular interactions in a crystal **1**: (*a*) skewed stacks, short contacts between molecules are shown, corresponding to C−H . . . π-stacking interaction, (*b*) a fragment of a molecule layer, showing hydrogen bonds C−H. . .F.

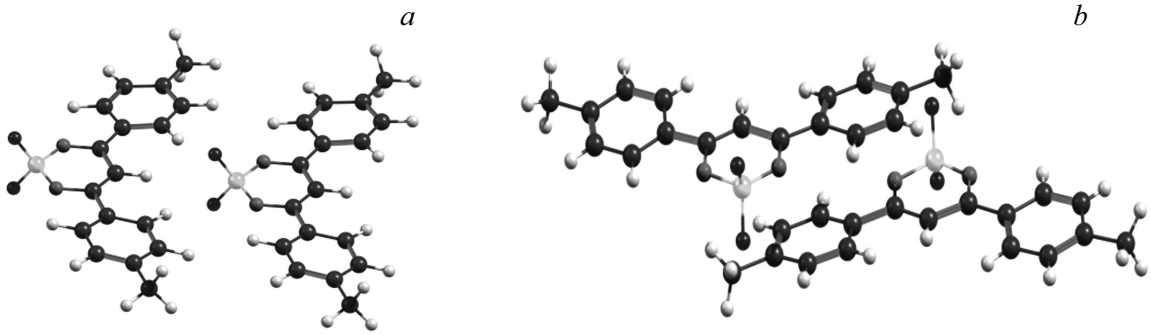


Figure 7. Structure of dimers in a crystal **1**: (*a*) „head−head", (*b*) „head−tail".

with the experimental geometry is higher than that with the optimal geometry by 0.03 at.units

Conclusions

The J-aggregates formation processes during dissolution of **1** crystals and their subsequent dissociation by absorption and luminescence spectroscopy and quantum-chemical modeling have been studied.

The results of the study showed that the process of dissolution **1** consists of three stages: 1) separation of fragments of at least 3−5 molecules from a crystal (the minimum amount for J-aggregates formation) and their solvation; 2) splitting of J-aggregates into individual solvated molecules; 3) molecule transition to a state corresponding to minimum of energy. The first stage (actual dissolution of a crystal) lasts for few minutes. For the second stage, several hours are already required, due to which it is possible to observe J-aggregates in the absorption spectrum of dilute solutions.

Funding

The work has been performed under the state assignment of the Ministry of Science and Higher Education of the Russian Federation (topic № 0205-2021-0001).

References

[1] A. Sakai, M. Tanaka, E. Ohta, Y. Yoshimoto, K. Mizuno, H. Ikeda. Tetrahedron Lett. **53**. 4138 (2012). DOI: 10.1016/j.tetlet.2012.05.122
[2] A.G. Mirochnik, B.V. Bukvetskii, E.V. Gukhman, V.E. Karasev. J. Fluoresc. **13** (2). 157 (2003). DOI: 10.1023/A:1022939209971
[3] X. Zhang, R. Lu, J. Jia, X. Liu, P. Xue, D. Xua, H. Zhoua. Chem. Commun. **46**. 8419 (2010) DOI: 10.1039/C0CC03448G
[4] H. Wu, L. Xue, Y. Shi, Y. Chen, X. Li. *Langmuir*. **27** (6). 3074 (2011). DOI: 10.1021/la104888p
[5] A.G. Mirochnik, E.V. Fedorenko, D.H. Shlyk, V.E. Karasev. Rus. J. Phys. Chem. **81** (11). 1880 (2007). DOI: 10.1134/S0036024407110295]
[6] Y.L. Chow, C.J. Johansson. J. Phys. Chem. **99** (49). 17566 (1995).
[7] W.A. Morris, T. Butle, M. Kolpaczynska, C.L. Fraser. Mater. Chem. Front. **1**. 158 (2017). DOI: 10.1039/C9QM00518H
[8] T. Butler, W.A. Morris, J. Samonina-Kosicka, C.L. Fraser. ACS Appl. Mater. Interfaces. **8**. m242 (2016). DOI: 10.1021/acsami.5b09688
[9] A.G. Mirochnik, E.V. Fedorenko, V.E. Karasev. Russ. Chem. Bull **57** (6). 1190–1193 DOI: 10.1007/s11172-008-0149-x]
[10] E.V. Fedorenko, A.G. Mirochnik, I.B. Lvov, V.I. Vovna. Spectrochim. Acta A. **120**. 119 (2014). DOI: 10.1016/j.saa.2013.10.016
[11] B.V. Bukvetskii, E.V. Fedorenko, A.G. Mirochnik. Russ. Chem. Bull. **62** (9). 1991 (2013). DOI: 10.1007/s11172-013-0289-5]
[12] G. Weber. Biochem. J. **75** (2). 335 (1960). DOI: 10.1042/bj0750335
[13] A.G. Mirochnik, E.V. Fedorenko. Opt. i spektr., **123**. № 3 (in Russian). P. 365 (2017). DOI: 10.7868/S0030403417090252 [A.G. Mirochnik, E.V. Fedorenko. **123** (3) 365 (2017) DOI: 10.1134/S0030400X17090247]
[14] B.V. Bukvetskiy, E.V. Fedorenko, A.G. Mirochnik, A.Yu. Beloliptsev Zhurn. struktur. khimii. (in Russian).**53** (1). 139 (2012) [B.V. Bukvetskii, E.V. Fedorenko, A.G. Mirochnik, A.Yu. Beloliptsev. J. Struct. Chem. **53** (1) (2012). DOI: 10.1134/S002247661201009X]
[15] M.W. Schmidt, K.K. Baldridge, J.A. Boatz. et al. J. Comput. Chem. **14** (11). 13 (1993). DOI: 10.1002/jcc.540141112
[16] E.V. Fedorenko, A.G. Mirochnik, A.Yu. Beloliptsev. J. Lumin. **196** (4). 316 (2018). DOI: 10.1016/j.jlumin.2017.12.071
[17] P. Pringsgame. Fluorescence and phosphorescence. M.: Izd-vo inostrannoy literatury, p. 1951. 622 .[P. Pringsheeim. Fluorescence and Phosphorescence. New York–London, 1949]
[18] A.I. Kitaigorodsky. Molekulyarnyye kristally. M.: Nauka, 1971. p. 424 (in Russian).
[19] D. Rohde, C.-J. Yan, L.-J. Wan. Langmuir. **22** (10). 4750 (2006) DOI: 10.1021/la053138+