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CRYSTAL STRUCTURE AND LUMINESCENCE OF 2,2-DIFLUORO-4-(4′-PHENYLPHENYL)-6-METHYL-1,3,2-DIOXABORIN ($C_6H_5C_6H_4COCHCOCH_3BF_2$)

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The crystal structure of 2,2-difluoro-4-(4′-phenylphenyl)-6-methyl-1,3,2-dioxaborin ($C_6H_5C_6H_4COCHCOCH_3BF_2$) (**1**) is determined. The effect of the π-stacking interaction on the luminescent properties of compound **1** at 300 K and 77 K is shown.

Keywords: β-diketonates of boron difluoride, 2,2-difluoro-4-(4′-phenylphenyl)-6-methyl-1,3,2-dioxaborin, crystal structure, excimers, luminescence.

β-Diketonates of boron difluoride exhibit intense luminescence both in solutions and crystals [1]. 2,2-Difluoro-4-(4′-phenylphenyl)-6-methyl-1,3,2-dioxaborin ($C_6H_5C_6H_4COCHCOCH_3BF_2$) (**1**) is a representative of the class of benzoylacetonates of boron difluoride with a substituent in the phenyl ring. We have previously studied the effect of α-substituent on the spectral and luminescent properties of crystalline benzoylacetonates of boron difluoride [2]. A change in the number of alkyl substituents, which does not affect the luminescent properties of a single molecule, results in a change in the supramolecular architecture of the crystal. At the same time, the luminescent properties of the crystals also change significantly [3]. The luminescence spectrum of crystalline **1** was found to be bathochromically shifted as compared to other studied benzoylacetonates. Thus, it is of interest to study the causes of the bathochromic shift in the luminescence spectrum. Supposed causes are: 1) a change in the supramolecular architecture of the crystal; 2) an increase in the π electron system of the molecule. The aim of this single crystal X-ray diffraction study of compound **1** is to determine the possible dominant effect of one of the above reasons.

Experimental. Compound **1** was synthesized using the double acylation method by passing boron trifluoride gas through the diphenyl solution in acetic anhydride [4]. The crystals of compound **1** were obtained for single crystal X-ray diffraction analysis by recrystallization from toluene on slow cooling of the solution.

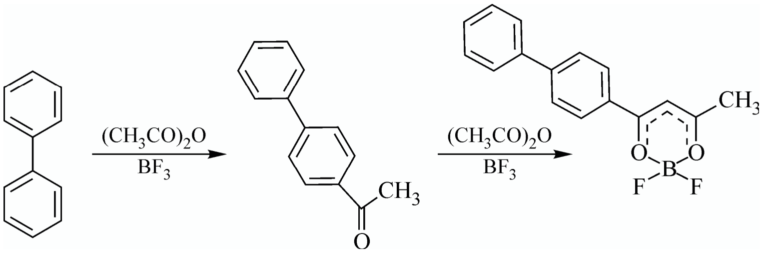

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TABLE 1. Crystallographic Data, Characteristics of the Diffraction Experiment, and Refinement Parameters for the Structure of Compound **1**

Parameter	Value
Empirical formula	$C_{16}H_{13}BF_2O_2$
Molecular weight	286.07
Radiation wavelength, Å	0.71073
Space group	$P2(1)/c$
a, b, c, Å	8.233(1), 12.410(2), 13.592(2)
β, deg	91.347(2)
V, Å^3; Z	1388.4(3), 4
$d_{x.}$, g/cm^3	1.369
μ, mm^{-1}	0.106
F(000)	592
Crystal dimensions, mm	0.21×0.12×0.10
Data collection over θ, deg	2.22-30.06
Ranges of reflection indices	$-11 \le h \le 8$, $-15 \le k \le 17$, $-18 \le l \le 19$
Measured reflections	10,864
Independent reflections	40,242 [R(int) = 0.0366]
Completeness, %	98.9
Refinement method	least squares method against F^2
S	0.944
R factors over $I > 2\sigma(I)$	$R1 = 0.0449$, $wR2 = 0.1181$
R factors over all reflections	$R1 = 0.0862$, $wR2 = 0.1368$
Extinction coefficient	0.0019(17)
Residual electron density (max/min), e/Å^{-3}	0.188/–0.172

The luminescence spectra were measured at 300 K and 77 K using an SDL-1 spectrometer ($\lambda_{excit} = 365$ nm). The kinetics of the luminescence decay was measured on a FluoTime 200 (PicoQuant) laser picosecond spectrfluorimeter.

The single crystal X-ray diffraction study was performed on a SMART-1000 Bruker CCD system at 293(2) K. The experimental data were collected in three groups of 906 frames each at φ = 0°, 90°, and 180° respectively, ω-scanning with a step of 0.2° and 20 s exposure for each frame. The data were edited, the unit cell parameters were refined, and the integral intensities were recalculated into the structural amplitude modules using the programs [5]. The structure was solved by the direct method with further refinement of positional and thermal parameters in the anisotropic approximation for all non-hydrogen atoms using the programs [6]. Positions of hydrogen atoms were well revealed in the electron density synthesis, however, they did not contain any new information, therefore, for the subsequent study we used those calculated and refined in the riding model. The crystal chemical data have been deposited with the Cambridge Crystallographic Data Center under No. CCDC 735612, which is available on request at www.ccdc.cam.ac.uk/data_request/cif. The main crystallographic parameters of the studied sample, characteristics of the single crystal X-ray diffraction experiment, and details of the structural model refinement by the least squares method are listed in Table 1, while interatomic distances are presented in Table 2. The structure of the molecule of **1** is shown in Fig. 1.

Results and Discussion. The crystal structure of the studied compound is based on isolated molecules of 1 (Fig. 1). A crystallographically independent molecule multiplied by the nearest symmetry center and translation in the [100] direction makes stacks of molecules with parallel orientation that are infinite along the *a* crystallographic axis. The stack multiplied by the *c* glide reflection plane is parallel to the initial one, while the molecular planes are oriented at an angle of 67.56 (0.03)° against the initial ones. Hence, the molecules of **1** are packed in a tile- stack arrangement. The infinite stacks of molecules are combined into a three-dimensional framework by the van der Waals interaction. Molecules of the neighboring stacks have F…H and O…H bifurcated bonds that are described for the boron difluoride complexes in the work [7].

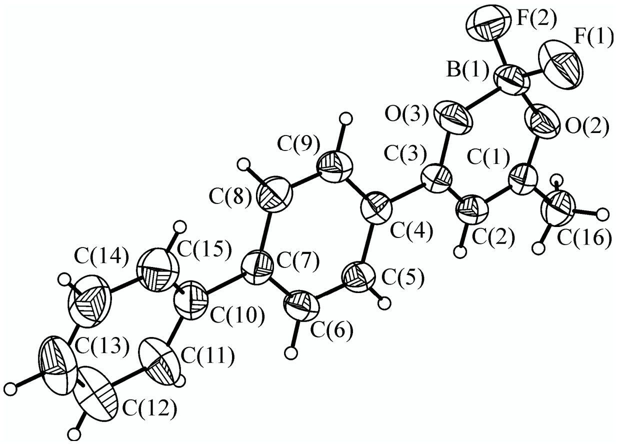

Fig.1. Molecular structure of compound **1**.

TABLE 2. Bond Lengths of Compound **1** (*l*, Å)

Bond	*l*	Bond	*l*	Bond	*l*	Bond	*l*
B(1)–F(1)	1.361(2)	C(2)–C(1)	1.370(2)	C(7)–C(6)	1.391(2)	C(11)–C(12)	1.383(2)
B(1)–F(2)	1.364(2)	C(2)–C(3)	1.379(2)	C(7)–C(8)	1.395(2)	C(13)–C(12)	1.356(3)
B(1)–O(2)	1.480(2)	C(4)–C(3)	1.468(2)	C(8)–C(9)	1.375(2)	C(13)–C(14)	1.372(3)
B(1)–O(3)	1.479(2)	C(4)–C(5)	1.394(2)	C(7)–C(10)	1.488(2)	C(15)–C(14)	1.381(2)
C(1)–O(2)	1.297(2)	C(4)–C(9)	1.391(2)	C(10)–C(11)	1.385(2)	C(1)–C(16)	1.481(2)
C(3)–O(3)	1.297(2)	C(5)–C(6)	1.377(2)	C(10)–C(15)	1.393(2)		

A molecule of **1** consists of two aromatic rings and one quasi-aromatic (chelate) ring. The C–O and C–C bonds of the chelate ring are leveled in pairs; bond lengths correspond to one-and-a-half bonds (Table 2). First and the second phenyl ring planes are at an angle of 23.85°, while the second phenyl and chelate ring planes are at 9.09°. As the CCDC data analysis shows, in the crystalline state, a diphenyl molecule has an angle between the phenyl rings when one of them participates in the formation of π bonds or π–π stacking interaction, for instance [8, 9]. In other cases, the diphenyl molecule is planar [10-12]. In compound **1**, the C(3)–C(4) bond is shorter than C(7)–C(10) (Table 2), which indicates a higher conjugation of π systems of the second phenyl and chelate rings than that of two phenyl ones. An increase in the C–C bond length of the second phenyl ring in comparison to the first one also shows that π electrons of the first phenyl ring hardly participate in the π system of the molecule. It seems that in order to evaluate the effect of the first phenyl ring as well as the substituent in benzoylacetonate of boron difluoride, it is necessary to evaluate only its inductive effect. Indeed, an extension of the molecular π system should cause a bathochromic shift of the luminescence maximum in single molecules [13], and the luminescence band maximum of a dilute solution of **1** is 425 nm as is also for benzoylacetonates of boron difluoride with the alkyl substituent in the *para*-position of the phenyl ring [3].

The stack arrangement is shown in Fig. 2. The stack has two types of overlapping: in one case, all three rings of interacting molecules participate in the π stacking interaction, in the other case, only the chelate ring and the phenyl ring bonded to it. The maximum π–π stacking interaction is observed when the interacting molecules overlap completely: the second phenyl rings are coplanar and located at a distance of 3.44 Å. The distance between the first phenyl and chelate ring planes located at 14.76° to each other is 3.47-4.02 Å. If the plane overlapping is not complete, the phenyl and chelate rings that participate in the π stacking interaction are located at 9.39°, and the distance between them is 3.45-3.62 Å. All types of the π stacking interaction facilitate the formation of pre-excimer positions in the crystals of **1** [14].

The effective π–π stacking interaction causes a significant bathochromic shift of the luminescence band in the crystals of **1** in comparison to other studied benzoylacetonates [15]. Various π–π stacking interaction types provide the

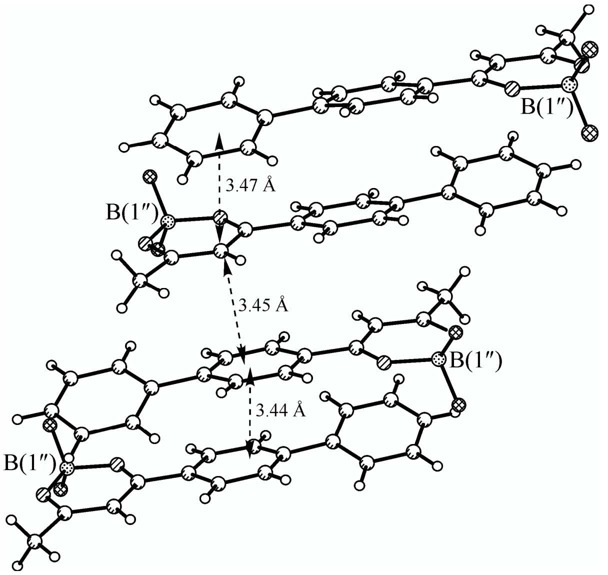

Fig. 2. Stack fragment in the crystal of **1.**

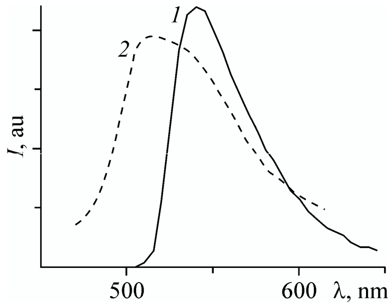

Fig. 3. Luminescence spectra of the crystals of **1**: 300 K (*1*), 77 K (*2*).

existence of several luminescent centers in the crystal of **1**. Indeed, as the study of the kinetics of the luminescence decay shows, the kinetics is two exponential with the life time τ_1 = 19.0 ns (23.92%) and τ_2 = 5.5 ns (76.08%). The presence of two luminescent centers is supported by the measurements of the luminescence spectrum at low temperatures (Fig. 3): when the temperature is lowered, there is a distinct hypsochromic shift of the luminescence spectrum maximum (30 nm), and the second band appears. As shown previously in [16], these changes in the luminescence spectrum occur if with a temperature decrease to 77 K the repulsive forces are most important in the stacking interaction, which hinders the occurrence of excimer fluorescence. In the crystals of **1** with complete overlapping of the neighboring molecules (3.44 Å) the distance between the second phenyl rings corresponds to the minimum intermolecular distance at which the excimer formation is possible [17]. The temperature decrease to 77 K is likely to cause crystal compression resulting in shortening of this distance, strengthening of the intermolecular repulsion, and the hypsochromic shift of the luminescence spectrum.

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