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Nitrogen-Containing Analog of Dibenzoylmethanate of Boron Difluoride: Luminescence, Structure, Quantum Chemical Modeling, and Delay Fluorescence

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Abstract Boron difluoride of 3-amino-1,3-diphenyl-2propene-1-onate (1) has been synthesized and its crystal structure has been determined. The comparative studies of 1 and its oxygen analog 1,3-diphenyl-1,3-dionate (dibenzoylmethanate) of boron difluoride (2) have been performed using the methods of stationary and time-resolved spectroscopy and quantum chemical modeling. It was established that at the transition from solutions to crystals, a bathochromic shift of the spectra and a significant increase of luminescence intensity of 1 take place. The luminescent properties of solutions of 1 and 2 are similar. The peculiarities of crystal packings of 1 and 2 are responsible for differences in crystals luminescent properties. For crystals of 2, one observes the luminescence of J-aggregates and excimers, while for 1, in which a dimer is an elementary structural fragment, only the excimer luminescence is registered. A delayed excimer fluorescence of the P-type was observed for crystals of 1 and 2 at room temperature. The intensity of the delayed fluorescence of 1 is 300-fold higher than that of 2.

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Introduction

Recently, the number of published works devoted to studies of physical-chemical properties of B-diketonates of boron difluoride has increased significantly [1-7]. There appeared works related to development of functional polymers, in which β -diketonates of boron difluoride were used as photoconducting units in organic solar cells [8], novel luminescing biopolymers that allow studying living cells by means of multiphoton microscopy [9-11], and brightly luminescing polymeric materials characterized with good film-forming properties [12]. A noticeable increase of the number of publications is mainly concerned with unique luminescence and photochemical properties of compounds of this interesting class: intensive luminescence of solutions and crystals over the whole visible and IR ranges and the ability to form excimers [13, 14] and exciplexes [15, 16]. An interesting class of luminophors is composed of nitrogen-containing analogs of boron difluoride *β*-diketonates characterized with aggregation-induced emission (AIE) and crystallizationinduced emission: boron difluoride β-ketoiminates have weak luminescence in solutions [17, 18], but are intensive luminophors in the crystalline state [18, 19]. Due to this, the studies of the relationship between the crystal structure and spectral-luminescent properties of boron difluoride ketoiminates is an interesting objective. The number of researched boron difluoride ketoiminates is limited: for the most part spectral-luminescent properties of compounds bearing bulky substituents at the nitrogen atom (phenyl, tret-butyl,

para-bromophenyl, para-methoxyphenyl) are described [4, 18]. At the same time, in the work [19] boron difluoride enaminedibenzoylmethanate was taken as an example to demonstrate that the presence of methyl substituent at the nitrogen atom considerably affects molecular structure. However, due to an AIE, ketoiminates and diiminates of boron difluoride in crystalline state appear to be effective luminophores [20-22]. The AIE materials have varieties of high-tech applications in the fields of light-emitting devices, chemical sensors, and biological probes [23-25]. In the present work, a comparative study of 3-amino-1,3-diphenyl-2-propene-1-onate of boron difluoride (1) and its oxygen analog 1.3-diphenylpropan-1.3dionate (dibenzoylmethanate) of boron difluoride (2) (see scheme 1) has been performed using the methods of stationary and time-resolved spectroscopy and quantum chemistry simulation.

Experimental

Instrumentation and Methods

Absorption spectra of chloroform solution of **1** and **2** were registered on a Shimadzu-UV2550 spectrometer in a quartz cell (light path: 10 mm). Luminescence and excitation spectra of chloroform solution of 1 and 2 were registered on a Shimadzu-RF5301 spectrometer in a quartz cell (light path: 10 mm). A solution of naphthalene in ethanol was used as a standard for measuring the fluorescence quantum yield ($\varphi = 0.12$). Solvents were obtained from EKOS-1 and were used without additional purification.

IR spectra (KBr disks) were recorded on the Shimadzu IR Prestige-21. NMR spectra (CDCl₃) were measured on the Bruker WH 400. Mass spectra were recorded in the positive and negative ion modes (electrospray ionization ESI, a Shimadzu LCMS-2010EV mass spectrometric detector); the samples were injected in the system acetonitrile – water (9: 1).

Fluorescence lifetime measurements by time-correlated single-photon counting (TCSPC) were performed on a FluoTime 200 device (PicoQuant) with a PDL 800-B (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.

The fluorescence and phosphorescence spectra as well as the delayed fluorescence lifetime of the crystals were measured on a Varian Cary Eclipse spectrofluorimeter.



The images of crystals were obtained by fluorescence microscopy using the microscope AXIOPLAN-2 Imaging (Carl Zeiss, Germany) in standard configuration, filter set 02 (excitation 365 nm, FT 395, LP420) [26].

The set of diffraction reflections was obtained in the Center for collective use of scientific equipment of the Kurnakov Institute of General and Inorganic Chemistry RAS using an automatic Bruker APEX-II CCD diffractometer APEX2, SAINT, and SADABS programs were used at collection and processing of the reflection data array [27]. The structure was determined using the direct method and refined using the fullmatrix least-squares method of the software complex SHELX [28]. Non-hydrogen atoms were refined in the approximation of anisotropic thermal vibrations. Hydrogen atoms are localized in the difference synthesis and refined in the isotropic approximation. The crystallographic data for compound **1** were deposited with Cambridge Crystallographic Data Center (CCDC 1455004) and can be obtained upon request at www.ccdc.cam.uk./data_request/cif.

Polyethylene (PE) films doped with the compound **1** were prepared according to [29]. Polyethylene powder (low density, 500 μ m, Alfa Aesar) and the complex **1** (0.5 wt.%) were mixed thoroughly and compacted using a hydraulic press (*p* = 8 MPa, *T* = 130 °C).

Materials

1,3-Diphenyl-2-propene-1-onate of boron difluoride (2) was prepared and purified according to [30].

Synthesis of 3-Amino-1,3-diphenyl-2-propene-1-on

The solution of 1 g of **2** (0.00367 mol) in 30 mL of acetonitrile was added to 1.4 mL (0.011 mol) of ammonia solution (25 %) and stirred for one hour. The reaction mixture was extracted with chloroform and washed with water. Then, the solvent was evaporated. The formed oil was rubbed up with a few hexane drops. The formed fine crystalline precipitate was recrystallized from the isopropanol – water mixture (yield 0.7 g, 84 %). IR (KBr), ν/cm^{-1} : 3365, 1593, 1525, 1481. Anal. found: C, 80.67, H, 5.90, N 6.29 %; calc. For C₁₅H₁₃NO: C, 80.69, H, 5.87, N 6.27 %. ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 10.42 (s, NH₂), 7.96–7.93 (m, 2H), 7.65–7.62 (m, 2H), 7.48–7.43 (m, 6H), 6.15 (s, 1H).

Synthesis of 3-Amino-1,3-diphenyl-2-propene-1-onate of Boron Difluoride (1)

A mixture of 1 g (0.0045 mol) of 3-amino-1,3-diphenyl-2propene-1-on and 2 mL of boron trifluoride etherate (0.009 mol) in a absolute toluene was stirred on a magnetic stirrer at 125 °C. The formed precipitate was filtered, washed with toluene, and recrystallized from an isopropanol-

Scheme 1 Sructures of 3-amino-1,3-diphenyl-2-propene-1-onate of boron difluoride (1) and 1,3-diphenyl-1,3-dionate of boron difluoride (2)

acetonitrile mixture (m = 0.9 g, 73 % yield, m.p. 204–206 °C). IR (KBr), ν/cm^{-1} : 3350, 1612, 1581, 1519, 1492, 1375, 1120, 1053 cm⁻¹. MS: (ESI+) m/z 272; (ESI-) m/z 270. Anal. found: C, 66.19, H, 4.83, N 5.17 %; calc. For C₁₅H₁₃BF₂NO: C, 66.22, H, 4.82, N 5.15 %. ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 8.04–8.02 (m, 2H), 7.75–7.73 (m, 2H), 7.65–7.48 (m, 6H), 6.54 (s, 1H).

Computational Details

Quantum chemistry simulations of electron absorption spectra of compounds in different conformations were performed in a cluster approximation using GAMESS program complexes [31]. The structural parameters, energy characteristics, and electron structures of compounds were determined at full geometry optimization in the basis 6-311G (d,p) by the nonempirical method and the density functional method with the exchange-correlation potential B3LYP. The compounds electron absorption spectra with taking into account excited singlet and triplet states were calculated by the TDDFT method in the basis 6-311G(d, p) with the potential B3LYP.

Results and Discussion

The ligand of 3-amino-1,3-diphenyl-2-propene-1-on was obtained through the interaction of dibenzoylmethanate of boron difluoride (2) with ammonia at room temperature. The synthesis of 3-amino-1,3-diphenyl-2-propene-1-onate of boron difluoride (1) was carried out according to the modified method [32].

The luminescence and excitation spectra of the diluted solutions of 1 and 2 in chloroform are very similar (Fig. 1a). Thus, the maximum of luminescence spectrum of solution 2 (417 nm) coincides with that of 1, whereas the quantum yield of luminescence for 1 is much lower than that for 2 ($\varphi(1) = 0.03$; $\varphi(2) = 0.3$).

The absorption spectra of 1 and 2, unlike the excitation spectra of these compounds, demonstrate some differences. For instance, the absorption spectrum of solution 1 $(\lambda_{\text{max}} = 352 \text{ nm})$ is shifted to the blue range relative to that of solution **2** ($\lambda_{\text{max}} = 365 \text{ nm}$) (Fig. 1b).

It is of importance that the spectra of absorption and excitation of 1 are identical, unlike those of 2. Differences in absorption and excitation spectra can be related to changes in the molecule geometry in the excited state.

For 1 the absorption spectra in the optimized geometry of the ground state and the structurally relaxed state (SRS) were calculated, and the comparison of theoretical and experimental absorption spectra was performed (Table 1).

Quantum chemical calculations of the absorption spectra of 1 for the geometry of the ground state are in good agreement with the experimental spectra (Table 1). The absorption spectrum of 1 for the ground state has an intensive band at 330 nm, and the maximum of experimental absorption spectrum of 1 in chloroform is located at 352 nm. The long-wavelength component of absorption spectrum corresponds to the HOMO - LUMO transition with the redistribution of electron density from the chelate ring and the phenyl cycle at the oxygen atom over the whole molecule (Fig. 2a). The calculated absorption spectrum of 1 in the geometry of SRS has a significant bathochromic shift relatively to that in the ground state and is in good agreement with the experimental excitation spectrum (Table 1).

Molecule 1 acquires a flatter structure in the SRS geometry, as compared to the ground state one. Here, torsion angles undergo changes: in the ground state geometry the phenyl ring at the nitrogen atom deviates from the chelate cycle plane by an angle of 38.68° , whereas in the SRS geometry this angle is equal to 14.278° (Fig. 2b). One should mention changes in the LUMO structure of 1 (Fig. 2a).

Coincidence of excitation and absorption spectra of 2 results from the fact that the geometry of its molecule (unlike 1) does not undergo significant changes at transition from the ground state to the excited one [33]. Here, according to [33] in molecule 2, the electron density is homogeneously







 Table 1
 Absorption maxima of experimental and calculated spectra and excitation maxima of 1

Absorption spectra			Excitation spectra* λ , nm
Calculated spectra		Experimental spectra* λ , nm	
Ground state λ , nm (f)	SRS λ , nm (f)		
266 (0,132)	279 (0,206)	263	250
330 (0,544)	385 (0,448)	352	365, 380

* in chloroform (C = 10^{-5} mol/L)

distributed over two phenyl rings and the chelate cycle, which creates a united π -system over the whole molecule. Unlike molecule **2**, in the ground state of molecule **1** the phenyl ring at the nitrogen atom, according to quantum chemistry calculations, is excluded from the system of molecule π -conjugation (Fig. 2b). However, at transition from the ground state to the excited one, the molecule of **1** becomes flatter, while the electron density is delocalized over the whole molecule (see Fig. 2). Thus, similarity of excitation spectra of **2** and **1** is explained by similar geometric structures of molecules of these compounds in the excited state.

The data of quantum chemical calculations are corroborated by those of X-ray structural analysis, according to which the molecule of 1, unlike that of its oxygen analog 2 [34], has a non-flat structure: both phenyl rings are turned relatively to the chelate cycle (Fig. 3): the torsion angle O - C(1) - C(4) - C(4)C(5) is equal to 12.82°, whereas the angle N - C(3) - C(10) - C(10C(15) – to 29.91 The molecule of **2** is virtually coplanar: the planes of phenyl rings are at angles of 3.08° and 3.54° to that of the chelate cycle [34]. A large divergence of the phenyl substituent at the nitrogen atom from the chelate ring plane in the molecule of 1 is caused by steric hindrances created by the hydrogen atom near the nitrogen atom. In the chelate cycle of 1, unlike β -diketonates of boron difluoride [34–36], one observes the distortion of the quasi-aromatic character: the C(3) - N bond length (1.314 Å) corresponds to the length of the double bond, while the C(1) - O bond length (1.320 Å) is equal to the length of the single C - O bond in the phenol molecule [37] and the C(2) - C(3) bond length is larger than

that of the C(1) - C(2) bond (they are equal to 1.418 and 1.372 Å, respectively).

The dependencies of luminescence and excitation spectra of solutions **1** on concentration were investigated (see Figs 4a and b). In the excitation spectrum of a diluted solutions of **1** in chloroform ($C = 10^{-7} - 10^{-5}$ mol/L), one observes a band with a maximum at 365 nm (Fig. 4a). At the concentration increase up to 10^{-4} mol/L, in the excitation spectrum one observes a narrow band with a maximum at 385 nm, which shifts to 390 nm upon concentrating. Similar concentration dependence of excitation spectra for **2** was investigated in detail in [38].

The registration of the luminescence spectrum of **1** was carried out at λ_{max} of the excitation (365, 385, and 390 nm for solutions with $C = 10^{-7} - 10^{-5}$, 10^{-4} , and $C = 10^{-3}$ mol/L, respectively) (Fig. 4b). The luminescence increases 3-fold when the solution concentration of **1** increases from 10^{-7} to 10^{-6} mol/L.

Upon the solution concentration increase up to 10^{-5} mol/L, the increase of the luminescence intensity slows down, which is related to the process of concentration quenching (the luminescence intensity increases just 1.4-fold) (Fig. 4b). Upon further concentrating of the solution of 1 (C = $10^{-4} - 10^{-3}$ mol/L), one also observes luminescence quenching in the maximum of the excitation spectrum of the monomeric luminescence ($\lambda_{ex} = 365$ nm). However, during excitation in the absorption spectrum long-wavelength range, there occurs a dramatic increase of the luminescence intensity of the solution of 1: at C = 10^{-4} mol/L ($\lambda_{ex} = 385$ nm) – in 3 times relatively to the solution with C = 10^{-5} mol/L; at

Fig. 2 Frontier molecular orbitals (a) and molecular geometry (b) of 1 in the geometry of ground and structurally relaxed states





Fig. 3 Molecular structure of 1

 $C = 10^{-3} \text{ mol/L} (\lambda_{ex} = 385 \text{ nm}) - \text{ in } 2 \text{ times relatively to the solution with } C = 10^{-4} \text{ mol/L} (Fig. 4b).$

The dependence of the efficiency of concentration quenching on the exciting light wavelength is described in [39] and was explained by formation of intermolecular aggregates excited by the wavelength different from that of the maximum of the absorption spectrum of individual molecules. As was shown earlier in [38, 40] in case of β -diketonates of boron difluoride such phenomenon is related to formation of weakly bound aggregates.

An additional confirmation of possible formation of aggregates of 1 consists in the comparison of its absorption and excitation spectra in PE film and concentrated solution in chloroform (Fig. 5a).

As was shown earlier [38, 40], the luminescence of concentrated solutions of β -diketonates of boron difluoride concentrated solutions was caused by formation of brightly luminescent aggregates. Here, low concentration of aggregates in solutions results in the fact that, in most cases, one observes just a low-intensity long-wavelength shoulder in the absorption spectrum. Unfortunately, the solubility of β -diketonates of boron difluoride in organic solvents does not allow attaining the concentration value sufficient for registering aggregates in the absorption spectrum. In the course of replacement of the 'good' solvent by the 'bad' one, the system becomes unstable and fast complex crystallization takes place, which makes the study much more complicated. In the polymer matrix, unlike the solution, the mobility of molecules decreases and the possibility of registering of aggregates emerges.

Figure 5a shows the absorption and excitation spectra of 1 in PE film. The maximum of the excitation spectrum of 1 in the PE film corresponds to the long-wavelength shoulder of absorption of J-aggregates in the absorption spectrum at 385 nm. The maximum of the excitation spectrum in PE (385 nm) coincides with that of the narrow excitation band in concentrated solutions (Fig. 5a), which allows its assignment to aggregate excitation.

Thus, at the concentration of the solution of **1** insufficient for registering aggregates in the absorption spectrum, more sensitive luminescence method registers the formation of aggregates, whose excitation spectrum is present in the longwavelength range of the absorption spectrum. As a result, the effect of the internal filter observed for the monomeric luminescence does not interfere with registration of the aggregate luminescence.

A bathochromic shift of the luminescence maximum by 100 nm is observed in luminescence spectra of **1** (Fig. 5b) at the transition from solutions to crystals. In the excitation spectrum of the crystals, just like in that of the concentrated solutions and PE film (Fig. 5a), one observes a narrow intensive long-wavelength band of aggregate excitation (Fig. 5b). In case of β -diketonates of boron difluoride, the substantial bathochromic shift of the luminescence spectrum observed at transition from solutions to crystals is often related to the excimer luminescence [38, 40].

Time-resolved luminescence spectra were registered for the crystals of 1 (Fig. 6). In the course of time, the intensity of the luminescence short-wavelength band decreases, whereas that of the long-wavelength one increases. A comparative analysis of stationary luminescence spectra of crystals and solutions of 1 (Fig. 5b) allows the assignment of the short-wavelength band (445 nm) in the time-resolved spectrum to monomer luminescence and of the long-wavelength one (525 nm) to excimer luminescence.

Fig. 4 Excitation spectra $(\lambda_{reg} = 420 \text{ nm})$ (**a**) and luminescence spectra (**b**) of chloroform solutions of **1**





Fig. 5 a Spectra of 1 in solution (C = 10^{-3} mol/L, chloroform) and in PE film (0.5 % mass): absorption spectra of 1 in PE film (*1*) and in solution (2), excitation spectra of 1 in PE film ($\lambda_{reg} = 495$ nm) (3) and in solution ($\lambda_{reg} = 420$ nm) (4). b Normalized spectra of 1 in solution

Analysis of the crystal structure of **1** demonstrates that the formation of excimers is facilitated by the presence of an effective stacking-interaction (Fig. 7). The molecules of **1** in the crystal form dimers consisting of antiparallel molecules, between which C-H... π - and π - π -stacking interactions take place. In their turn, such dimers are bonded to each other through the π - π -stacking interaction (Fig. 7a). The N-H ... F-B (3.01 Å) hydrogen bond emerges between adjacent molecules of **1**, the NHF bond angle is equal to 159.6° (Fig. 7b).

In the dimer, a partial π - π -overlapping of chelate cycles of adjacent molecules takes place: the distance between molecules is equal to 3.67 Å, which is an optimal one for excimer formation [41]. The distance between the hydrogen atom and the phenyl ring plane at C-H... π -interaction is equal to 2.69 Å (Fig. 7c).

According to the X-ray structural analysis data, in the crystal structure of 1 dimers form J-aggregates of the 'brickwork' type [42]: phenyl rings of each of the dimer molecules participate in the π - π -stacking interaction with phenyl rings of two adjacent molecules located to the left and to the right (Fig. 7a).

The crystal structure of **2** corresponds to that of J-aggregates of the 'brickwork' type, but, unlike the case of **1**, the



Fig. 6 Time-resolved luminescence spectra of crystal 1



(C = $1 \cdot 10^{-5}$ mol/L, chloroform) and in crystal: luminescence spectra of crystal ($\lambda_{ex} = 430$ nm) (1) and solution ($\lambda_{ex} = 365$ nm) (3), excitation spectra of crystal ($\lambda_{reg} = 490$ nm) (2) and solution ($\lambda_{reg} = 420$ nm) (4)

elementary unit here is not a dimer, but an individual molecule [38]. The peculiarities of the crystalline packing of 1 and 2serve as the reason of the difference of luminescence properties of crystals (Fig. 8). In the luminescence spectra of the crystals of 2, one observes, unlike 1, not only the excimer luminescence (530 nm), but also a short-wavelength band of the luminescence of J-aggregates (470 nm) (Fig. 8c) [38]. Indeed, the data of the time-resolved spectroscopy show that the kinetics of luminescence of the crystals of 2 is different at different wavelengths: at $\lambda_{\text{lum}} = 470 \text{ nm } \tau_1 = 25.6 \text{ ns}$ (66.61 %); $\tau_2 = 0.5 \text{ ns}$ (6.16 %); $\tau_3 = 1.5$ ns (27.23 %); at $\lambda_{\text{lum}} = 530$ nm $\tau_1 = 13.0$ ns (97.39 %). In the structure of 2, in which an individual molecule rather than a dimer serves as an elementary unit, excimer traps are absent. As was show in [43], the formation of the excimers of 2 is observed only on the crystal surface defects (Fig. 8b). At the same time, in the case of 1, where a dimer is an elementary structural unit, one observes only the excimer luminescence (500 nm) (Fig. 8a, c). The kinetics of the luminescence of crystals of 1 is mono-exponential: $\tau = 22.4$ ns. At comparing the luminescence properties of 1 and 2, one should mention a significant bathochromic shift of the maximum of the excimer luminescence of 2 relatively to 1 (530 and 500 nm, respectively). A flat structure of the molecule of 2 facilitates more efficient π - π -overlapping of the interacting molecules and the excimer formation.

For crystals of 1 at room temperature, an intensive delayed fluorescence (490 nm) was observed at room temperature; the spectrum also contains a long-wavelength band (615 nm) attributed to the crystals phosphorescence (Fig. 8c). The maximum of delayed fluorescence coincides with that of excimer luminescence of crystals of 1 (see Figs 5b and 8c). The measured lifetime of the delayed fluorescence of crystals of 1 was 0.15 ms, while the lifetime of phosphorescence (615 nm) could not be determined with an acceptable accuracy due to its low intensity. Since no dependence of the intensity of the observed delayed fluorescence of 1 on temperature was

Fig. 7 Crystal structure of 1: a partial view detailing the stacking interactions, b view of F... H-N intermolecular interaction and c partial view detailing the C-H... π stacking interactions of dimer 1





Fig. 8 a – Fluorescence images of crystals of **1**. **b** – Fluorescence images of crystals of **2**. c – Normalized luminescence spectra of crystals **1** and **2** at 300 K: fluorescence spectra of **1** (I) and **2** (3), delayed fluorescence and phosphorescence spectra of **1** (2) and **2** (4)

revealed, it was concluded that it belonged to P-type which emerged as a result of triplet-triplet annihilation with excimer formation [44]. In the case of **2** one also observes a delayed fluorescence of excimers at room temperature (560 nm) (Fig. 8c). It is worth mentioning that although the fluorescence intensities of crystals of **1** and **2** are comparable, the intensity of the delayed fluorescence of **1** is 300-fold higher. The reason of a dramatic decrease of the intensity of the delayed fluorescence in crystals of **2** consist, probably, in the absence of excimer traps and, as a result, another way of deactivation of the excited state will be related to fluorescence of Jaggregates.

Conclusions

Boron difluoride 3-amino-1,3-diphenyl-2-propene-1-onate (1) has been synthesized and its crystal structure has been determined. The comparative studies of 1 and its oxygen analog 1,3-diphenyl-1,3-dionate (dibenzoylmethanate) of boron difluoride (2) have been performed using the methods of stationary and time-resolved spectroscopy and quantum chemical modeling. It was found that a bathochromic shift and a significant increase of the luminescence intensity occurred at transition from solutions to crystal of 1.

The molecule of 1, unlike that of its oxygen analog (2) has a non-flat structure: the presence of the hydrogen atom by that of nitrogen in the molecule of 1 blocks the coplanar positioning of phenyl and β -diketonate rings. Despite the differences in the molecules geometries, luminescent properties of the diluted solutions of 1 and 2 are similar. At the same time, the peculiarities of the crystalline packings of 1 and 2 are responsible for differences in their crystals spectralluminescent properties.

The flat structure of the molecule of **2** promotes more efficient π - π -overlapping of adjacent molecules, causes an efficient spreading of the local excitation over the whole crystal volume, and facilitates the formation of excimer traps only on the crystal surface defects. For crystals of **2**, one observes the luminescence of J-aggregates and excimers, while for **1**, in which a dimer is an elementary structural fragment, only the excimer luminescence is registered. Here, the flat structure of the molecule of **2** promoted more efficient π - π -overlapping of interacting molecules and a bathochromic shift of the maximum of the excimer luminescence of **2**, as compared to **1**.

For crystals of **1** and **2**, the delayed excimer fluorescence of the P-type was found at room temperature. The intensity of the delayed fluorescence of **1** is 300-fold higher than that of **2**.

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