Full Articles

Crystal structures and excimer fluorescence of anisoylbenzoylmethanatoboron and dianisoylmethanatoboron difluorides

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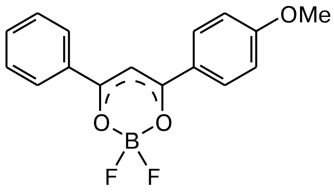
The crystal structures and spectral-luminescence properties of anisoylbenzoylmethanatoboron difluoride (**1**) and dianisoylmethanatoboron difluoride (**2**) were studied in the solid state and in solution. The structural features of compounds **1** and **2** are responsible for the occurrence of a new type of excimers in solutions, which differs from that observed in the crystalline state.

Key words: fluorescence, crystal structure, X-ray diffraction analysis, excimer, β-diketonatoboron difluorides.

Excimers (excited-state dimers) are one of the possible forms of existence of organic molecules in the excited state.[1,2] This phenomenon was studied in-depth by both experimental[3—5] and theoretical methods.[6,7] The state-of-the-art X-ray diffraction techniques can be used as a tool in studying the excimer nature of fluorescence of crystals.[8—10] Up to now, the structures of excimers of organic molecules have been studied primarily for the simplest compounds, *viz.*, arenes and indoles.

Earlier,[11—13] we have studied the relationship between the nature of luminescence and the crystal structures of compounds containing quasiaromatic heterocycles, *viz.*, β-diketonatoboron difluorides. In continuation of these investigations, in the present study we established the crystal structures of anisoylbenzoylmethanatoboron difluoride (**1**) and dianisoylmethanatoboron difluoride (**2**) and examined their excimer fluorescence.



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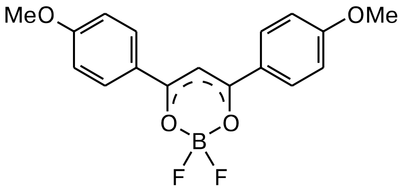

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Table 1. Selected bond lengths in molecules **1** and **2**

1		**2**	
Bond	d/Å	Bond	d/Å
B—O(1)	1.466(3)	B—O(1)	1.464(8)
B—O(2)	1.473(3)	C(2)—O(1)	1.318(7)
C(9)—O(1)	1.306(3)	C(1)—C(2)	1.368(7)
C(7)—O(2)	1.305(3)	C(2)—C(3)	1.453(9)
C(9)—C(8)	1.364(3)	C(6)—O(2)	1.376(7)
C(8)—C(7)	1.374(3)	C(9)—O(2)	1.426(9)
C(7)—C(4)	1.455(3)		
C(9)—C(13)	1.464(3)		
C(1)—O(3)	1.352(3)		
C(30)—O(3)	1.434(3)		

Table 2. Spectroscopic characteristics of compounds **1** and **2**

Compound	n	Solution		Crystal
		C_n/mol L^{-1}	λ_{fluor}/nm	λ_{max}/nm
1	1	0.2	449, 464, 505*	550
	2	0.01	434, 446, 463*	
	3	0.001	431, 445, 464*	
2	1	0.071	449, 479, 506*	529
	2	$5.7 \cdot 10^{-3}$	449, 470, 507*	
	3	$3.6 \cdot 10^{-5}$	432, 449, 474*	

* The result of the Gaussian expansion of the fluorescence spectrum into subcomponents using the MicroCal Origin program (Version 6.1).

Results and Discussion

According to the results of X-ray diffraction analysis, molecule **1** contains the distorted diketonate ring, in which the C(8)—C(7) bond length is larger than the C(8)—C(9) bond length and the B—O(2) bond length is larger than the B—O(1) bond length. The distance between the C(1)—C(6) phenyl ring containing the methoxy group and the diketonate ring is shorter than the distance between the C(12)—C(17) phenyl ring and the diketonate ring. The observed distortions in molecule **1** (Table 1, Fig. 1) are indicative of strong π-conjugation between the *p*-methoxyphenyl ring and the carbonyl group C(9)—O(1) of the β-diketonate ring. By contrast, X-ray diffraction study demonstrated that the bonds in molecule **2** are equalized, which is, apparently, indicative of the occurrence of more efficient π-conjugation throughout molecule **2** compared to molecule **1**. This fact is confirmed by the bathochromic shifts of the absorption maxima in the spectra of compound **2** relative to those in the spectra of compound **1** (Table 2).

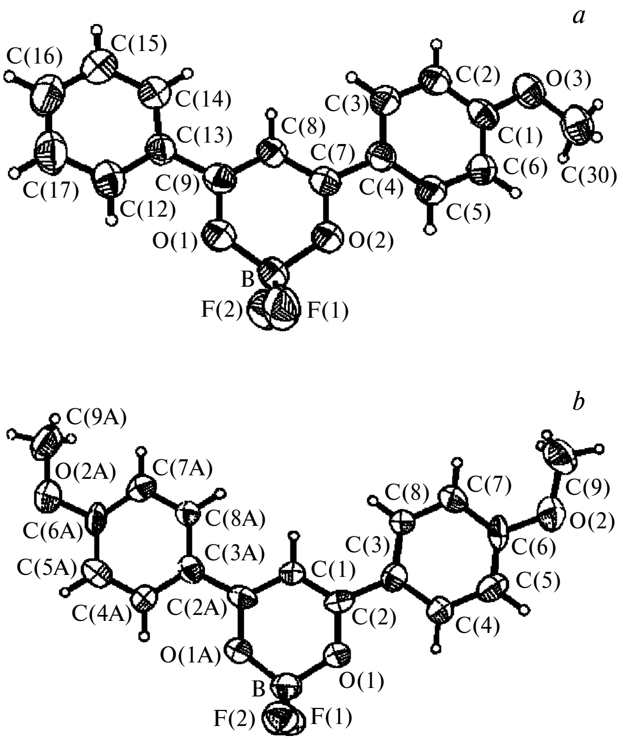


Fig. 1. Molecular structures of **1** (*a*) and **2** (*b*).

The presence of the MeO group in the second Ph ring leads to a change in the symmetry of the complex. As a result, molecule **2** has a twofold symmetry axis passing through the boron and γ-carbon atoms.

In the crystal of **1**, every four molecules are packed in stacks (Fig. 2). The first molecule overlaps with the second one and the third molecule overlaps with the fourth one in such a way that the C(1)—C(6) phenyl ring containing the MeO group of one molecule is located above the C(12)—C(17) ring of another molecule (see Figs. 1 and 2) (first type of overlapping). The degree of overlap is 27% of the surface area of the Ph ring; the distance between the planes is 3.55 Å. The second and third molecules in the stack are arranged in a different way: the diketonate ring of one molecule is located above the Ph ring containing the MeO group of another molecule (see Fig. 2) (second type of overlapping). The degree of overlap of each pair of the phenyl and diketonate rings is 67%; the distance between the planes is 3.58 Å.

In the crystal, molecules **2** are arranged in layers consisting of the parallel molecules; the distance between the layers is 3.52 Å (Fig. 3). The nearest molecules of the adjacent layers are antiparallel to one another and overlap in such a way that the diketonate ring of one molecule is located above the Ph ring of another molecule and vice versa (see Fig. 3). The overlapping molecules are arranged in a staircase fashion; the degree of overlap is 27% of the surface area of the Ph ring.

For the compounds under study, the fluorescence spectra of crystals and the fluorescence and absorption spectra of solutions in chloroform were recorded at 300 K. The spectroscopic characteristics of compounds **1** and **2**

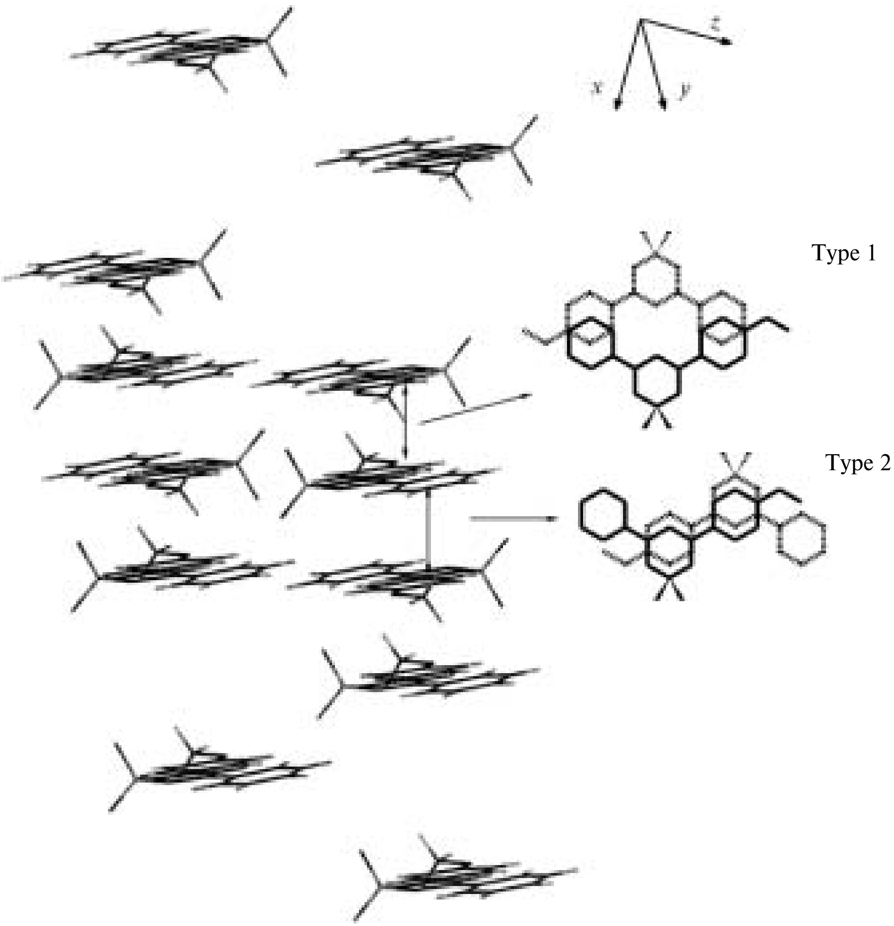


Fig. 2. Molecular packing of compound **1** in the crystal. The types of overlapping of the molecules are shown.

and the concentrations of the solutions are given in Table 2.

A substantial bathochromic shift of the fluorescence spectra is observed in going from solutions to crystals. For compounds **1** and **2**, the differences between the fluorescence maxima for a dilute solution and crystals are 119 and 97 nm, respectively (see Table 2). In addition, the fluorescence spectra of both compounds change as the concentration of the solution increases to the maximum possible value (C_1) (Fig. 4). In the spectrum of compound **1**, a new band with a maximum at 505 nm appears. For compound **2**, the spectral shape changes, and the

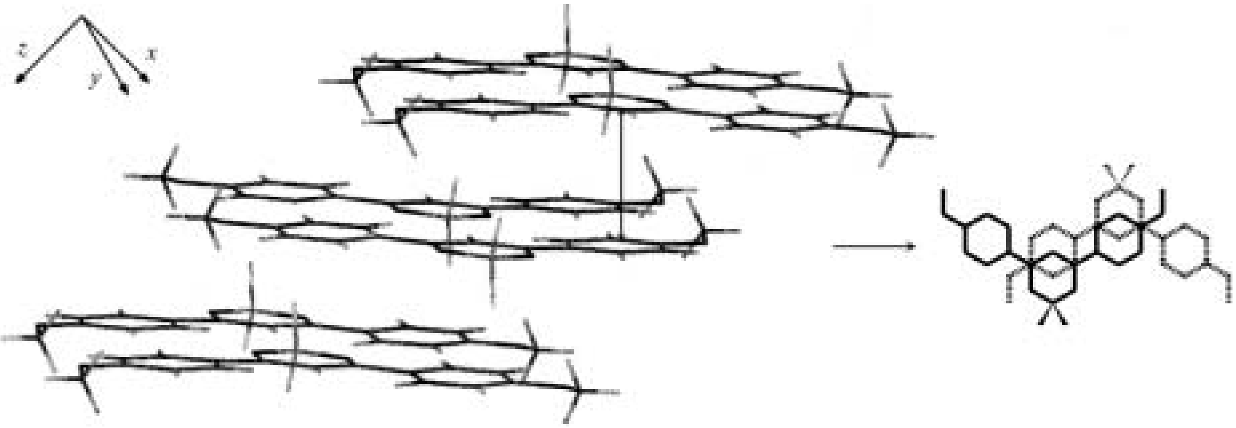


Fig. 3. Molecular packing of compound **2** in the crystal. The type of overlapping of the molecules is shown.

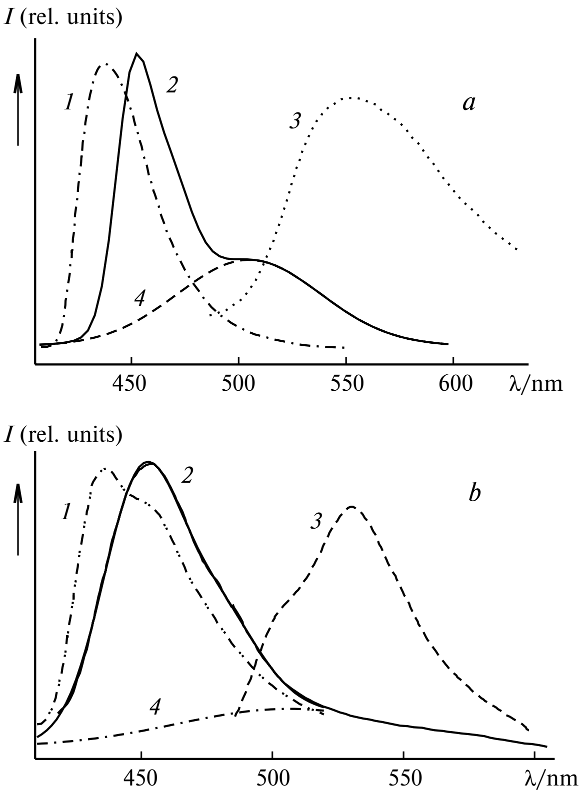


Fig. 4. Fluorescence spectra of dilute (*1*) and saturated (*2*) solutions, fluorescence spectra of the crystals (*3*), and the excimer fluorescence bands (*4*) of compounds **1** (*a*) and **2** (*b*).

Gaussian expansion of the fluorescence spectrum into subcomponents results in the appearance of a band with a maximum at 506 nm (see Table 2).

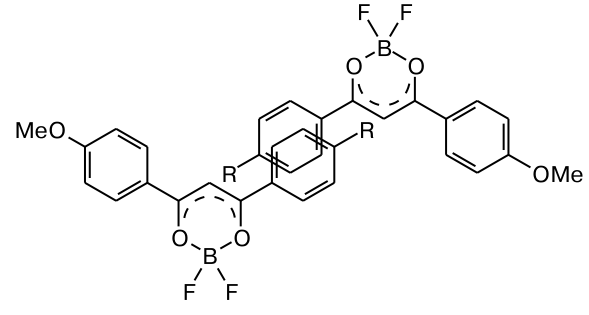
Based on comparative analysis of the fluorescence spectra of solutions of compounds **1** and **2** at different concentrations (see Table 2 and Fig. 4), only long-wavelength bands with maxima at 505 and 506 nm, respectively, in the spectra of solutions at high concentrations can be assigned to excimer fluorescence of both compounds, whereas short-wavelength bands can be assigned to luminescence from various vibrational-rotational levels of the excited state of individual molecules.[14]

In earlier studies,[11,13] we have found that the spectra of dibenzoylmethanatoboron and alkylbenzoylacetonatoboron difluorides in solutions have excimer fluorescence maxima identical to those observed in the spectra of crystals, which indicates that the excimers have the same structures in solutions and crystals. For the compounds considered in the presence study, the structures of excimers in solutions differ from those in the crystalline state.

The difference in the fluorescence spectra of excimers in solutions and crystals are associated with different modes of overlapping of interacting molecules.[15,16] For the phenyl and diketonate rings of interacting molecules in solutions of compounds **1** and **2** to overlap in a fashion identical to that observed in their crystals (see Figs. 2 and 3), a planar conformation of the molecules is required (this conformation is observed in the crystals of **1** and **2**). However, the molecules in solutions, unlike those in the crystalline state, are characterized by the existence of a set of rotational states, which decreases the probability of occurrence of a planar conformation. Unlike molecules **1** and **2**, the BF_2dbm molecules (dbm is dibenzoylmethane) in the crystals are packed in such a way that only the Ph rings of the nearest molecules overlap with each other[11] and the rotation of the phenyl rings about the bond between the rings does not hinder their overlapping when going to solutions.

In alkylbenzoylacetonatoboron difluorides,[13] both the phenyl and diketonate rings of the molecule are involved in formation of excimers. Hence, rotation of the Ph rings in solutions of these complexes can hinder overlapping of the molecules typical of the crystalline state. However, the excimer fluorescence maxima for these compounds in solutions are identical to those in the crystals. Apparently, the efficient overlapping of the phenyl and diketonate rings is hindered primarily due to steric effects associated with rotation of the bulky α-substituent. In alkylbenzoylacetonatoboron difluorides, rotation of the α-substituent (Me group) does not hinder overlapping of the phenyl and diketonate rings of the interacting molecules and the formation of excimers typical of the crystalline state.[13]

Unlike the compounds described earlier,[11,13] even a small rotation of the diketonate ring with respect to one of the Ph rings in molecules **1** and **2** results in steric hindrance to overlapping of the phenyl and diketonate rings of the interacting molecules upon the formation of excimers in solution. In the crystals, this optimum overlapping of the molecules takes place (see Figs. 2 and 3). Hence, the formation of excimers of another type (different from that present in the crystals) is more probable in solutions of molecules **1** and **2**. This type of excimers is associated with overlapping of only the Ph rings of two molecules, like that observed in BF_2dbm,[11] and can occur even in the case of a small rotation of the phenyl rings relative to the chelate ring.



R = H, OMe

Therefore, the structural features of molecules **1** and **2** and their crystal packings are responsible for the formation of a new type of excimers in solutions, which differs from that observed in the crystals. More efficient (by a factor of 2.5) overlapping of the π systems of the nearest molecules in the crystals of **1** compared to that in the crystals of **2** leads to a larger bathochromic shift of the fluorescence maximum in going from solutions to the crystals.

Experimental

Compound **1** was synthesized and purified according to a procedure described earlier.[17] The crystals were prepared by recrystallization from toluene.

Table 3. Crystallographic data, characteristics of X-ray data collection, and details of the structure refinement for anisoylbenzoylmethanatoboron difluoride **1** and dianisoylmethanatoboron difluoride **2**

Parameter	1	2
Molecular formula	$C_{16}H_{13}BF_2O_3$	$C_{17}H_{15}BF_2O_4$
Molecular weight	272.05	332.10
T/K	293(2)	293(2)
Space group	$P\bar{1}$	$C2/c$
a/Å	7.9652(10)	21.121(5)
b/Å	9.0211(12)	7.1542(17)
c/Å	10.7176(14)	10.432(3)
α/deg	75.583(3)	90
β/deg	80.738(3)	96.206(4)
γ/deg	69.756(3)	90
V/Å^3	697.41(16)	1567.0(7)
Z	2	4
ρ_{calc}/g cm^{-3}	1.438	1.408
μ/mm^{-1}	0.114	0.113
θ Scan range	1.97—32.44°	1.94—20.98°
Number of measured reflections	5517	2731
Number of independent reflections	3996	842
R_{int}	0.0324	0.1143
Number of refections with $I > 2\sigma(I)$	1172	353
Absorption correction	Based on crystal habitus	
Method of refinement	Least-squares against F^2	
Number of parameters in refinement	212	112
Goodness-of-fit S	0.734	0.852
R factors based on reflections with $I > 2\sigma(I)$		
R_1	0.0526	0.0648
wR_2	0.1156	0.1474
R factors based on all reflections		
R_1	0.1734	0.1563
wR_2	0.1507	0.1802
Extinction coefficient	0.009(3)	0.0030(11)
Residual electron density (min/max)/e Å^{-3}	−0.191 (0.187)	−0.284 (0.236)

Dianisoylmethanatoboron difluoride (2). Gaseous BF_3 was passed through a mixture of trifluoroacetic anhydride (0.2 mol), malonic acid (0.03 mol), and anisole (0.09 mol) with stirring on a cool bath (water—ice) until the reaction mixture was saturated. The mixture warmed up and an orange precipitate formed. Then water (100 mL) was added. The precipitate was filtered off and dried in air. After recrystallization from toluene, bright-yellow crystals were obtained in a yield of 5.0 g (44.75%), m.p. 209—210 °C. Calculated (%): C, 61.45; H, 4.52. $C_{16}H_{13}BF_2O_3$. Found (%): C, 61.53; H, 4.48.

The luminescence spectra of the crystalline compounds at 300 K were recorded on a SDL-1 spectrometer; the samples were irradiated with a DRSh-250 lamp (λ_{excit} = 365 nm). The fluorescence spectra of solutions were measured on a Shimadzu RF 5000 instrument.

X-ray diffraction study was carried out on a SMART-1000 CCD diffractometer (Mo-Kα radiation, λ = 0.71073 Å, graphite monochromator, crystal-to-detector distance was 45 mm). The X-ray data were collected using 606, 435, and 230 frames at ϕ = 0, 90, and 189°, respectively. The X-ray data were collected and processed, the unit cell parameters were refined, and the integrated intensities were converted into structure amplitudes using the SMART and SAINT-Plus programs.[18] The structure was solved by direct methods followed by the refinement of the positional and thermal parameters (with anisotropic thermal parameters for all nonhydrogen atoms) using the SHELXTL program package.[19] The hydrogen atoms were placed in calculated positions and refined using the riding model.

The principal crystallographic parameters, characteristics of X-ray diffraction data collections, and details of the structure refinement by the least-squares method are given in Table 3. The selected bond lengths are given in Table 1.

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