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Crystal structure and excimer fluorescence of dibenzoylmethanatoboron difluoride

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Fluorescence properties of dilute and concentrated solutions of dibenzoylmethanatoboron difluoride and its crystals were studied. Excimers are formed in concentrated solutions and crystals of dibenzoylmethanatoboron difluoride. The crystal structure of dibenzoylmethanatoboron difluoride was determined by X-ray diffraction analysis. It was found that the molecules of dibenzoylmethanatoboron difluoride are coplanar with an interplanar distance of 3.6 Å.

Key words: fluorescence, dibenzoylmethanatoboron difluoride, excimers, XRD, crystal structure.

An interest in studying the photophysical and photochemical properties of boron difluoride β-diketonates increased recently due to the possibility of using them as stuffs for the laser working substance, photocatalysts, and photocarriers for electrophotography.[1—3] Special attention is given to the photochemical properties of one of the most accessible and stable complexes, dibenzoylmethanatoboron difluoride (**1**). The kinetic studies of photoprocesses in solutions[4—7] and theoretical calculation of the molecular structure[8] have been performed for this compound. Despite this, luminescence of crystalline **1** was not studied up to now and the crystal structure of this compound remains unknown.

In continuation of our studies of a relation between the electronic structure and photophysical properties of dibenzoylmethanatoboron difluoride β-diketonates,[9] in this work we determined the crystal structure of **1** and performed the comparative study of fluorescence of its solutions and crystals.

Experimental

Dibenzoylmethanatoboron difluoride was synthesized by a described procedure[10] and recrystallized from an acetonitrile—toluene (1 : 1) mixture. Luminescence and luminescence excitation spectra of crystalline compounds were recorded at 77 and 300 K on a technique based on an SDL-1 spectrometer and an MDR-23 monochromator. DRSh-250 and Tungsram-2500 lamps served as excitation sources. Fluorescence and fluorescence excitation spectra were recorded on a Shimadzu RF 5000 instrument. UV spectra were recorded on a Hitachi 220A instrument.

The complete X-ray diffraction study was carried out on a SMART-1000 CCD instrument (Bruker) using MoKα radiation. Accumulation, data processing, refinement of unit cell parameters, and calculation of integral intensities to moduli of structural amplitudes were performed by known programs.[11] The structure was solved by the direct method followed by the refinement of positional and thermal parameters in the anisotropic approximation for all nonhydrogen atoms by published programs.[12] Positions of H atoms were revealed on electron density syntheses; however, calculated and refined positions in the "rider" model were used for structure refinement.

The main crystallographic parameters of the sample under study, characteristics of X-ray diffraction experiment, and refinement of the structural model by the least-squares method are presented in Table 1.

Results and Discussion

The molecular structure of **1** is shown in Fig. 1. The interatomic distances and bond angles are presented in Table 2. Molecule **1** is symmetric relatively to the axis crossing the B and C(8) atoms. The C—C and C—O bonds of the chelate cycle are leveled in pairs. The planes of the phenyl rings C(1)—C(6) and C(10)—C(15) are arranged at angles of 3.08° (0.28) and 3.54° (0.29), respectively, to the C(7)—C(9)—O(1)—O(2) plane. The B and C(8) atoms of the diketonate cycle shift from the molecule plane thus distorting it according to the "boat" type. The angles between the planes drawn through the atoms C(7)—C(8)—C(9), C(7)—C(9)—O(1)—O(2) and BO(1)—O(2), C(7)—C(9)—O(1)—O(2) are 176.25° (0.29) and 163.85° (0.80), respectively. A similar geometry of the chelate cycle was found for a molecule of acetylacetonatoboron difluoride.[13]

The structure of crystals **1** is presented by molecules forming a three-dimensional framework due to the van der Waals interaction (Fig. 2). The unit cell contains four parallel molecules of **1** arranged in pairs, and the phenyl rings of two adjacent molecules are localized one above another at a distance of 3.6 Å, which indicates a possibility of the interaction of π-orbitals. In the crystal cell molecules of **1** are arranged in such a way that only

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Table 1. Crystallographic data, characteristics of X-ray diffraction experiment, and refinement of the structure of molecule **1**

Parameter	Value
Formula	$C_{15}H_{11}BF_2O_2$
Molecular weight	272.05
Temperature/K	293(2)
Wavelength/Å	MoKα (0.71073)
Space group	$P2_1/n$
a/Å	6.9098(12)
b/Å	13.993(2)
c/Å	13.753(2)
β/deg	101.367(4)
Z	4
ρ_{calc}/g cm^{-3}	1.386
μ/mm^{-1}	0.109
F(000)	560
Crystal shape, mm	needle 0.14×0.18×0.22
Region of data collection over θ	2.91 − 20.02°
Intervals of reflection indices	$-6 \le h \le 6$, $-13 \le k \le 13$, $-11 \le l \le 13$
Measured reflections	4176
Independent reflections	1219 (R_{int} = 0.0324)
Reflections with $I > 2\sigma(I)$	649
Absorption	By cutting
Refinement method	Full-matrix least-squares by F^2
Refinement variables	182
S	0.942
R factors by $I > 2\sigma(I)$	$R_1 = 0.0511$, $wR_2 = 0.1416$
R factors by all reflections	$R_1 = 0.0945$, $wR_2 = 0.1648$
Molar absorption coefficient	0.018(16)
Residual electron density min/max) /e · Å^{-3}	−0.185/0.176 (near atom F(2))

the phenyl rings of two adjacent molecules are overlapped (by 41%).

Electronic absorption, fluorescence excitation, and fluorescence spectra were obtained for complex **1**.

The absorption spectra of a solution of **1** in chloroform and its powder in the polyethylene matrix are presented in Fig. 3. Based on the quantum-mechanical calculations of the absorption spectra of **1** in the gas phase,[14] we can propose the following assignment of bands in the absorption spectrum of a solution of **1** in chloroform: the band at 380 nm corresponds to π—π*-transitions of the electron density delocalized over the whole molecule; the band at 284 is assigned to π—π*-transitions related to the redistribution of the electron density from the Ph groups to the chelate ring (charge transfer band). The positions of bands in the UV spectrum of the chloroform solution and powder in the polyethylene matrix differ insignificantly, and the intensities of the bands are redistributed. The short-wave band has the maximum intensity in the UV spectrum of the powder of **1** in the polyethylene matrix, and the intensity of the long-wave band is maximum in the UV spectrum of a solution of **1**.

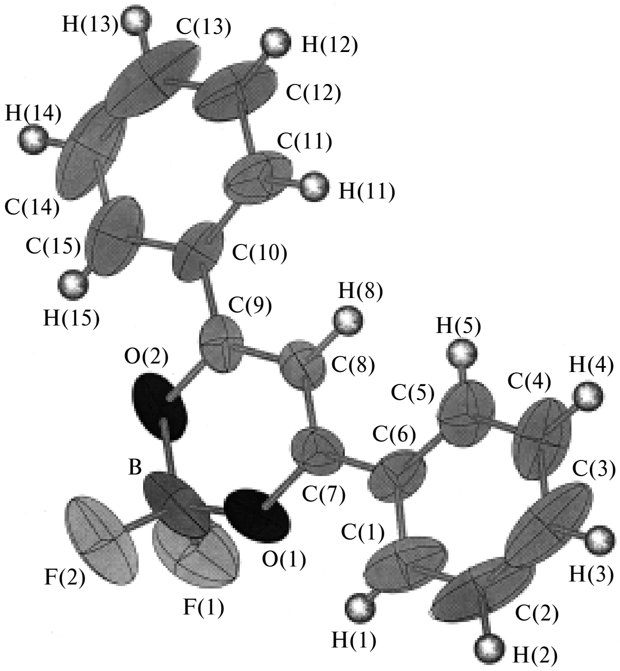

Fig. 1. Molecular structure of **1**.

Two bands are observed in the excitation spectrum of dilute solutions of **1** ($C = 10^{-3}$—10^{-4} mol L^{-1}). Both bands are localized in the spectral region corresponding

Table 2. Main bond lengths (d) and bond angles (φ) in molecule **1**

Bond	φ/Å
F(1)—B	1.362(7)
F(2)—B	1.348(6)
O(1)—B	1.486(7)
O(2)—B	1.478(7)
C(1)—C(2)	1.399(8)
C(2)—C(3)	1.343(9)
C(3)—C(4)	1.339(8)
C(5)—C(4)	1.376(6)
C(6)—C(1)	1.383(6)
C(6)—C(5)	1.371(6)
C(6)—C(7)	1.469(5)
C(7)—C(8)	1.377(5)
C(9)—C(8)	1.382(5)
O(1)—C(7)	1.298(4)
O(2)—C(9)	1.290(4)
C(9)—C(10)	1.457(6)
C(10)—C(11)	1.388(6)
C(10)—C(15)	1.374(6)
C(11)—C(12)	1.372(7)
C(12)—C(13)	1.359(8)
C(15)—C(14)	1.379(8)
Angle	φ/deg
F(2)—B—F(1)	111.9(5)
F(1)—B—O(2)	108.7(6)
F(1)—B—O(1)	108.9(6)
F(2)—B—O(2)	108.5(6)
F(2)—B—O(1)	107.8(5)

Angle	φ/deg
O(2)—B—O(1)	111.0(4)
C(3)—C(2)—C(1)	119.1(7)
C(3)—C(4)—C(5)	120.4(6)
C(4)—C(3)—C(2)	121.7(8)
C(5)—C(6)—C(1)	118.8(4)
C(6)—C(5)—C(4)	120.1(5)
C(6)—C(1)—C(2)	119.9(6)
C(1)—C(6)—C(7)	119.8(5)
C(5)—C(6)—C(7)	121.4(4)
O(1)—C(7)—C(6)	115.6(4)
O(1)—C(7)—C(8)	119.6(4)
C(7)—O(1)—B	122.1(4)
C(8)—C(7)—C(6)	124.7(5)
C(8)—C(9)—C(10)	124.0(4)
O(2)—C(9)—C(10)	116.3(4)
C(9)—O(2)—B	122.5(4)
O(2)—C(9)—C(8)	119.7(4)
C(7)—C(8)—C(9)	121.9(4)
C(11)—C(10)—C(9)	121.9(4)
C(15)—C(10)—C(9)	120.0(5)
C(10)—C(15)—C(14)	120.8(6)
C(13)—C(14)—C(15)	119.4(7)
C(12)—C(11)—C(10)	121.0(5)
C(13)—C(12)—C(11)	119.2(6)
C(14)—C(13)—C(12)	121.4(7)
C(15)—C(10)—C(11)	118.2(5)

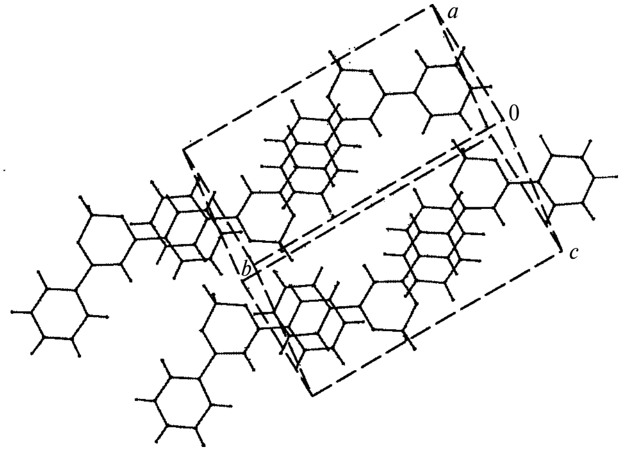

Fig. 2. Crystal structure of **1**.

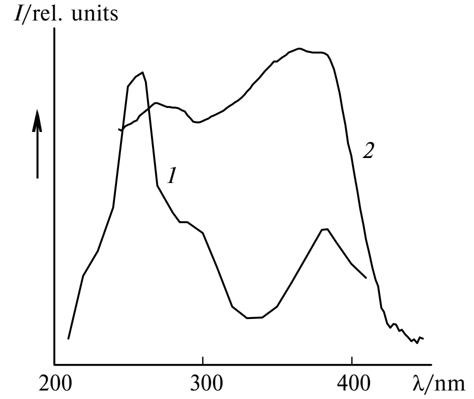

Fig. 3. Absorption spectra of **1**: *1*, powder in polyethylene matrix; *2*, solution in chloroform.

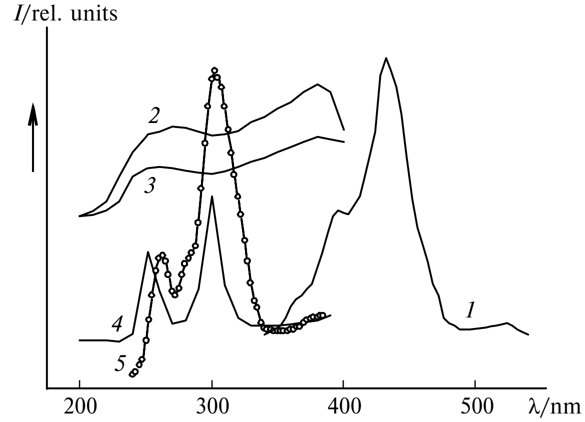

Fig. 4. Fluorescence excitation spectra of crystals (*1*) and solutions of **1** in chloroform (*2—5*): C (mol L^{-1}) = 0.9 (*2*), 0.1 (*3*), 10^{-2} (*4*), and 10^{-4} (*5*).

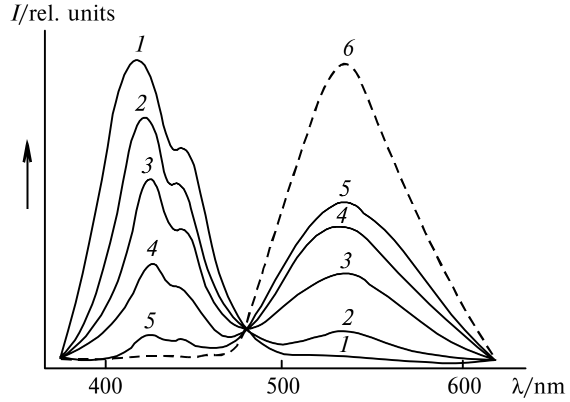

Fig. 5. Normalized fluorescence spectra of solutions of **1** in chloroform (*1—5*): C (mol L^{-1}) = 0.8 (*1*), 0.4 (*2*), 0.2 (*3*), 0.1 (*4*), 10^{-3} (*5*), and of crystals **1** (*6*).

to the position of the charge transfer band in the UV spectrum (284 nm). At the same time, a band corresponding to the long-wave component of the UV spectrum (380 nm) is absent from the excitation spectrum. When the concentration increases, the excitation spectra change (Fig. 4): the structured spectrum is transformed into the diffuse spectrum, and the narrow long-wave component (302 nm) disappears simultaneously with the appearance of a broad band with a maximum at 380 nm corresponding to the π—π^*-transitions of the electron density localized over the whole molecule.

Thus, electron transitions related to the charge transfer from the phenyl ring to the chelate cycle of an individual molecule are responsible in dilute solutions for fluorescence excitation, whereas on going to the concentrated solutions and crystals, fluorescence is excited by transitions of the electron density delocalized over the whole molecule, which is related to the enhancement of the intermolecular interaction.

The maximum of the fluorescence band of crystals **1** is bathochromically shifted by 116 nm relatively to the maximum of the fluorescence band of a dilute solution ($C = 10^{-4}$ mol L^{-1}). When the concentration of solutions of **1** in chloroform increases ($C = 10^{-4}$—10^{-1} mol L^{-1}), the intensity of the fluorescence band in the short-wave spectral region decreases. Similarly to published results,[15] a broad structureless fluorescence band simultaneously appears in the long-wave spectral region and becomes more and more intense (Fig. 5). This band coincides with the fluorescence band of crystalline **1**.

No change in the position of maxima of absorption band is observed for the studied interval of concentrations of **1**. Therefore, its molecules in the ground state are not associated. Hence, we assigned the new emission band to excited dimers (excimers), which are formed by the interaction of the excited and nonexcited molecules of **1**, and the geometry of excimers corresponds to the arrangement of molecules in crystal. Analysis of the crystal structure (see Fig. 2) shows that the excimers have an incomplete sandwich structure.

Thus, the substantial change in the photophysical properties on going from dilute solutions to concentrated solutions and crystals is a result of the specific features of the interaction of molecules of **1** and formation of the photoexcited excimer.

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