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Crystal structure and fluorescence properties of *p*-nitrobenzoylanisoylmethane and its complex with boron difluoride

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The crystal and molecular structures of *p*- and *m*-nitrobenzoylanisoylmethanatoboron difluoride were determined. The spectral luminescence properties of these compounds were studied and compared.

Key words: β-diketones, nitrobenzoylanisoylmethanes, β-diketonatoboron difluorides, crystal structure, molecular structure, fluorescence.

Among β-diketones synthesized to the present time,[1—3] only few compounds possess an intense fluorescence in the visible region at room temperature. The exceptions are *p*- and *m*-nitrobenzoylanisoylmethanes. Fluorescence of the β-diketones themselves and their complexes with boron difluoride is of interest because β-diketonatoboron difluorides find use as stuffs of the laser working body, photocatalysts, and photoconductors for electrophotography.[4—6]

Continuing our studies of the structure and photophysical properties of β-diketonatoboron difluorides,[7] in this work we studied the crystal structures of *p*- and *m*-nitrobenzoylanisoylmethanes and *p*-nitrobenzoylanisoylmethanatoboron difluoride and their fluorescence properties.

Experimental

p-Nitrobenzoylanisoylmethane (**1**), *p*-nitrobenzoylanisoylmethanatoboron difluoride (**2**),[8] and *m*-nitrobenzoylanisoylmethane (**3**) were synthesized using previously published procedures and crystallized from a MeCN—toluene (1 : 1) mixture. Luminescence spectra of crystalline compounds were recorded on an SDL-1 spectrometer at 300 K. Fluorescence spectra of solutions were obtained on a JASCO FP-550 spectrophotometer. A solution of anthranilic acid in ethanol[9] was used as the standard for the measurement of the relative fluorescence quantum yield (φ) of solutions of compounds **1—3**. UV spectra were recorded on a Shimadzu UV-1201 instrument.

The X-ray diffraction study was carried out in a SMART-1000 CCD system (Bruker) using Mo-Kα radiation. Data were collected and selected and unit cell parameters were refined using known programs.[10] The structure was determined by the direct method followed by refinement of the positional and thermal parameters in the anisotropic approximation for all nonhydrogen atoms using previously published programs.[11] Positions of H atoms were revealed by the electron density syntheses. However, their calculated values refined by the riding model were used for the further work. The exceptions were the positions of the H atoms of the enole groups of compounds **1** and **3**, which were determined from the electron density syntheses and refined by the least-squares method.

The main crystallographic parameters of the samples, characteristics of X-ray diffraction experiment, and details of refinement of structural models by the least-squares method are presented in Table 1.

Results and Discussion

Molecular structures **1—3** are shown in Fig. 1. The main interatomic distances are presented in Table 2.

Crystalline dibenzoylmethane and its analogs with substituents in the phenyl rings exist in the enolic form,[2,12,13] including compound **1**. The parameters of the O(1)—H(1)···O(2) hydrogen bond are as follows: O(1)—O(2) 2.464(4), O(1)—H(1) 1.13(6), H(1)···O(2) 1.40(6) Å, and angle O(1)—H(1)—O(2) 152(5)°. Unlike compound **2** for which the C—C and C—O bonds of the chelate cycle are equalized in pairs, in molecule **1** the C(8)—C(9) bond is longer than the C(7)—C(8) bond and the O(1)—C(7) bond is longer than the O(2)—C(9) bond. The C(8)—C(9) and O(1)—C(7) distances are somewhat shorter than those for normal ordinary bonds, and the C(7)—C(8) and O(2)—C(9) bonds are longer than double bonds.[14] A similar pattern of bond lengths is observed for molecules of other β-diketones, in particular, dibenzoylmethane,[12,15] and indicates the conjugation between the C=C and C=O bonds of the enole molecule. At the same time, the molecular structure of compound **1** differs substantially from structures of other dibenzoylmethanes[2,12,15] because it is planar: the C(1)—C(6) and C(10)—C(15) planes of the phenyl rings are arranged at the 1.5(2) and 2.0(2)° angles, respec-

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Table 1. Crystallographic data, characteristics of X-ray diffraction experiment, and details of refinement of structures **1—3**

Parameter	**1**	**2**	**3**
Molecular formula	$C_{16}H_{13}NO_5$	$C_{16}H_{12}BF_2NO_5$	$C_{16}H_{13}NO_5$
Molecular weight	299.27	347.08	299.27
T/K	293 (2)	293 (2)	296 (3)
Radiation (λ/Å)	Mo-Kα (0.71073)	Mo-Kα (0.71073)	Mo-Kα (0.71073)
Space group	$P2_1$	$P2_1/c$	$Pca2_1$
a/Å	3.870(1)	13.159(3)	30.532(6)
b/Å	12.666(3)	12.526(3)	3.9274(8)
c/Å	14.408(4)	18.982(4)	11.615(2)
β/deg	95.309(5)	102.329(5)	—
$V/Å^3$	703.2(3)	3056.6(11)	1392.8(5)
Z	2	8	4
$\rho_{calc}/g\ cm^{-3}$	1.413	1.508	1.427
μ/mm^{-1}	0.106	0.126	0.107
F(000)	312	1424	624
Crystal size/mm^3	0.2S0.25S0.28	0.05S0.15S0.25	0.2S0.25S0.3
Region of data collection by θ/deg	3.22—23.27	2.20—23.53	2.20—21.74
Completeness (%)	99.1 (for θ = 23.27°)	99.9 (for θ = 23.53°)	99.8 (for θ = 21.74°)
Number of measured reflections	3125	14032	4495
Number of independent reflections	1683 (R_{int} = 0.0292)	4533 (R_{int} = 0.0942)	1765 (R_{int} = 0.0568)
Number of reflections with $I > 2\sigma(I)$	1401	1467	1440
Method of refinement	Full-matrix least-squares method by F^2	Full-matrix least-squares method by F^2	Full-matrix least-squares method by F^2
Number of refinement variables	205	454	202
S	0.992	0.744	0.981
R factors by $I > 2\sigma(I)$	$R_1 = 0.0433$, $wR_2 = 0.1031$	$R_1 = 0.0474$, $wR_2 = 0.0947$	$R_1 = 0.0445$, $wR_2 = 0.1000$
R factors by all reflections	$R_1 = 0.0534$, $wR_2 = 0.1096$	$R_1 = 0.1792$, $wR_2 = 0.1276$	$R_1 = 0.0568$, $wR_2 = 0.1043$
Residual electron density, $(\rho_{min}/e \cdot Å^{-3})/(\rho_{max}/e \cdot Å^{-3})$	0.008/1.544	−0.240/0.200	−0.168/0.137

tively, to the C(7)C(9)O(1)O(2) plane, which allows π-electrons of both phenyl rings to be involved in conjugation. It is most likely that this is precisely the coplanarity of both phenyl rings and the plane of the diketonate cycle of **1**, which favor intense fluorescence distinguishing this compound from other dibenzoylmethanes. In most other β-diketones, π-electrons of only one cycle are conjugated with the π-system of enole. In particular, in the case of dibenzoylmethane one of the phenyl rings turns by 16.9°, and another ring turns by 3.8°.[12,15]

When dibenzoylmethane is chelated, the C—C and C—O bonds of the chelate cycle are equalized and the phenyl rings turn by the 3.1(3) and 3.5(3)° angles to the plane of the chelate cycle.[16] During chelate formation of compound **1** the angles between the planes of the β-diketonate cycle C(8)C(10)O(1)O(2) and phenyl rings

Table 2. Main bond lengths for compounds **1—3**

Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å
Molecule **1**		Molecule **2A**		Molecule **2B**		Molecule **3**	
O(1)—C(7)	1.314(4)	C(10)—O(1)	1.302(5)	C(110)—O(101)	1.311(5)	O(2)—C(10)	1.304(5)
O(2)—C(9)	1.279(4)	C(8)—O(2)	1.309(5)	C(108)—O(102)	1.296(5)	O(1)—C(8)	1.283(5)
O(3)—N	1.217(4)	N(1)—O(5)	1.208(5)	N(101)—O(104)	1.210(5)	O(3)—N	1.223(5)
O(4)—N	1.221(5)	N(1)—O(4)	1.236(5)	N(101)—O(105)	1.226(5)	O(4)—N	1.228(5)
O(5)—C(13)	1.372(4)	C(2)—O(3)	1.352(6)	C(102)—O(103)	1.359(5)	O(5)—C(4)	1.358(5)
O(5)—C(16)	1.427(4)	C(1)—O(3)	1.449(5)	C(101)—O(103)	1.438(5)	O(5)—C(7)	1.417(5)
N—C(3)	1.472(5)	C(16)—N(1)	1.470(6)	C(116)—N(101)	1.467(6)	N—C(13)	1.466(6)
C(6)—C(7)	1.477(4)	C(10)—C(11)	1.484(6)	C(110)—C(111)	1.466(6)	C(10)—C(11)	1.501(6)
C(7)—C(8)	1.373(4)	C(9)—C(10)	1.355(6)	C(109)—C(110)	1.362(6)	C(9)—C(10)	1.364(6)
C(8)—C(9)	1.421(4)	C(8)—C(9)	1.375(6)	C(108)—C(109)	1.372(6)	C(8)—C(9)	1.410(6)
C(9)—C(10)	1.470(4)	C(7)—C(8)	1.455(6)	C(107)—C(108)	1.463(6)	C(1)—C(8)	1.453(6)

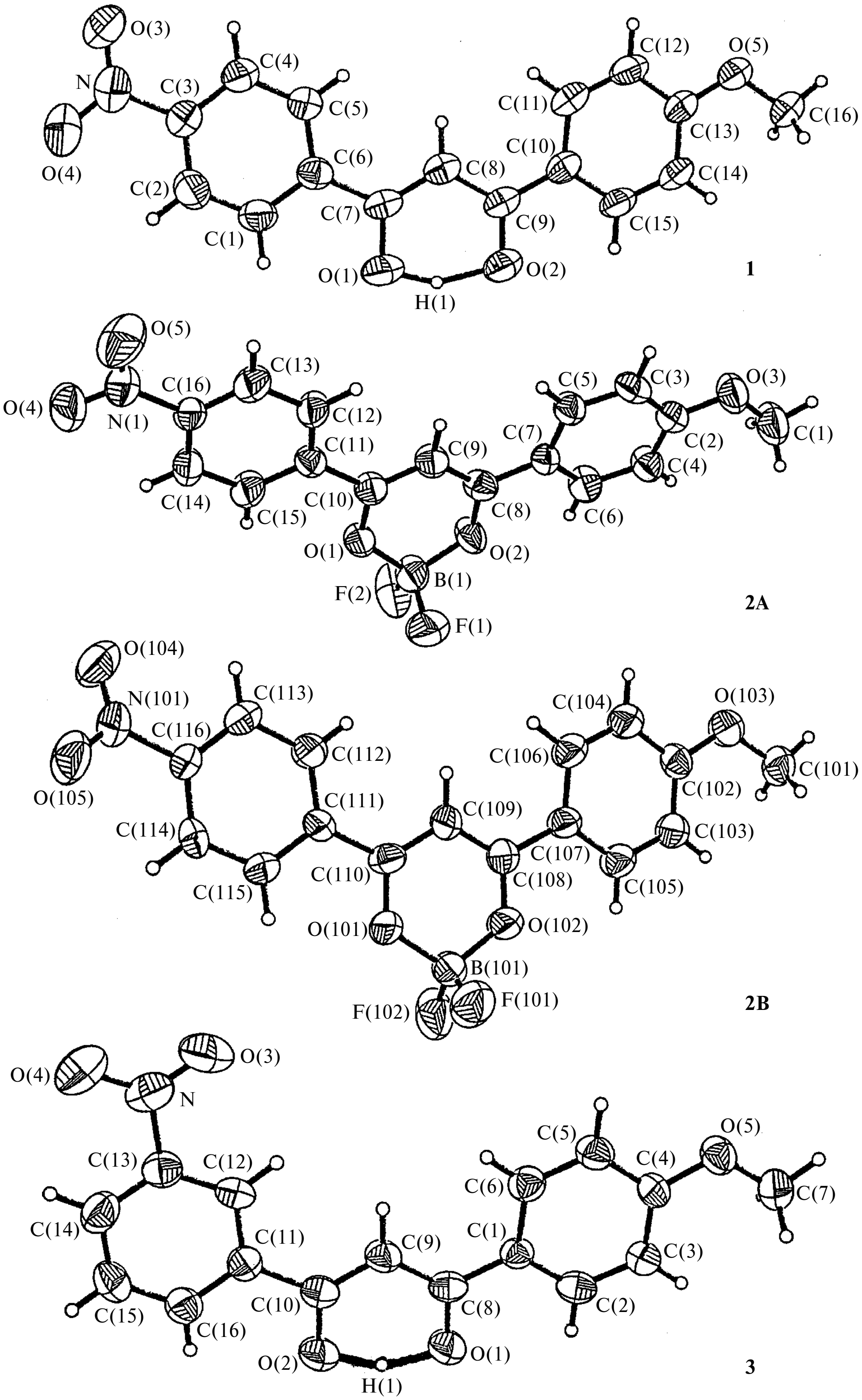

Fig. 1. Molecular structures of *p*-nitrobenzoylanisoylmethane (**1**), *p*-nitrobenzoylanisoylmethanatoboron difluoride (**2A**, **2B**), and *m*-nitrobenzoylanisoylmethane (**3**).

C(2)—C(7) and C(11)—C(16) increase to 8.2(4) and 9.4(4)°, respectively. On going from molecule **1** to molecule **2**, the orientation of the methoxy group relative to the phenyl ring remains almost unchanged but the C(7)—C(8) bond length (between the phenyl ring containing the methoxy group and the chelate cycle) in molecule **2** changes insignificantly compared to the C(9)—C(10) bond in molecule **1**, from 1.470 to 1.455 (1.463) Å. In addition, the symmetry of the N—O bonds in molecule **2** is distorted (N(1)—O(5) 1.208 Å; N(101)—O(104) 1.210 Å and N(1)—O(4) 1.236 Å; N(101)—O(105) 1.226 Å) compared to that in molecule **1** (N—O(3) 1.217 Å and N—O(4) 1.221 Å), and the angle between the N(1)—O(4)—O(5) and C(11)—C(16) plane increases to 10.8(9)° or that between the N(101)—O(104)—O(105) and C(101)—C(106) planes increases to 23.0(8)° compared to the angle of 6.8(5)° between the N—O(3)—O(4) and C(1)—C(6) planes in molecule **1**.

It is known[17] that when a molecule deviates from the planar structure, the probability of intramolecular conversion increases, which is manifested as the 1.6-fold decrease in the integral fluorescence of crystals **2** compared to crystals **1** (Fig. 2, *a*). The relative fluorescence intensities and positions of maxima of the absorption bands and the fluorescence intensities of the crystalline compounds and their solutions in chloroform are presented in Table 3. The fluorescence spectra of crystals **1** and **2** represent broad diffuse lines in a region of 470—660 nm (see Fig. 2, *a*). The positions of maxima and the shape of fluorescence bands of β-diketone and its complex with boron difluoride virtually coincide. The absorption spectra of compounds **1** and **2** in polyethylene are also close. These facts indicate that the structures and positions of HOMO and LUMO of *p*-nitrobenzoylanisoylmethane enole and its complex with BF_2 are close.

Table 3. Absorption (λ_{abs}/nm) and fluorescence (λ_{fl}/nm) spectra of crystalline compounds **1—3** (I) and their solutions in $CHCl_3$ (II)

Compound	λ_{abs} (logε)		λ_{fl} $(I_{rel})^a$ or $[\varphi]^b$	
	I^c	II	I	II
1	263, 364	260 (4.14), 370 (4.46)	535 (1.60)	520 [0.023]
2	263, 365	262 (4.11), 385 (4.43)	540 (1)	472 [0.020]
3	353	270 (4.23)^d, 360 (4.52)	523 (1.26)	485 [0.009]

[a] The fluorescence intensity of compound **2** was accepted as unity.
[b] Relative quantum yield.
[c] Films in polyethylene.
[d] Inflection.

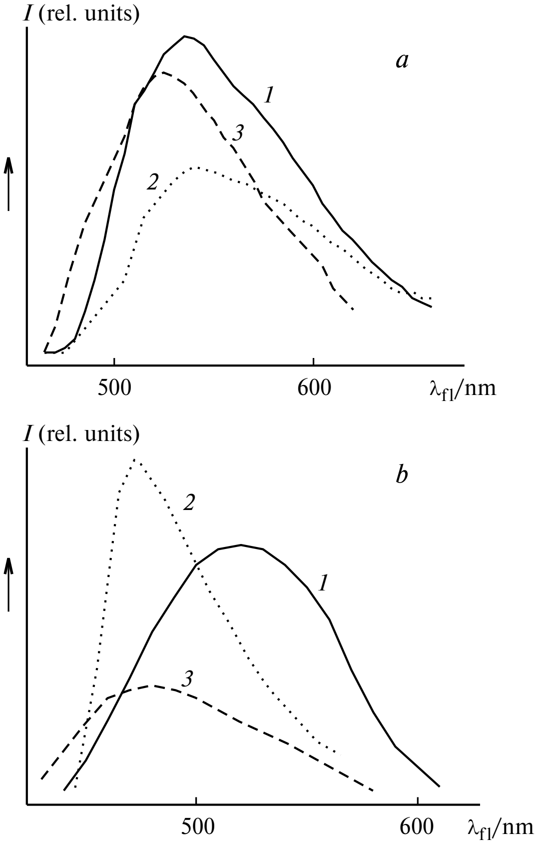

Fig. 2. Normalized fluorescence spectra of solutions ($3 \cdot 10^{-4}$ mol L^{-1}) (*a*) and crystals (*b*) of compounds **1—3** (*1—3*, respectively).

To reveal the role of the geometric factor in the formation of the fluorescence properties, we recorded the fluorescence spectrum of *m*-nitrobenzoylanisoylmethane (**3**), whose structure has previously been determined.[2] Crystal **3** contains[2] two different crystallographically independent molecules, which differ only in positions of the enolic H atom. The phenyl rings of these molecules are turned by 4.0(2)° (8.3(1)°) and 5.0(2)° (4.2(2)°) relative to the plane of the β-diketonate group. As a consequence, the fluorescence intensity of crystals **3** should be lower than that for compound **1**, whose molecules are planar. However, the fluorescence intensities of compounds **1** and **3** are close (see Table 3), which prompted us to perform an independent determination of the atomic structure of compound **3**.

The X-ray diffraction study of crystals **3**, unlike the previously published data[2] (where the authors studied monoclinic crystals of the same compound with the parameters $a = 13.050(3)$, $b = 15.975(3)$, $c = 14.425$ Å, $\beta = 111.16(3)°$, $Z = 8$, space group $P2_1/n$, and R factor by 1869 reflections with $I \geq 2\sigma(I)$ equal to 0.055) showed the orthorhombic system (see Table 1) with one independent *m*-nitrobenzoylanisoylmethane molecule.

The molecular structure of compound **3** is shown in Fig. 1. As in the case of compound **1**, molecules **3** exist in the enolic form, and the parameters of the O(1)—H(1)···O(2) hydrogen bond are the following: O(1)—O(2) 2.451(4), O(1)—H(1) 1.22(6), H(1)···O(2) 1.26(6) Å, and angle O(1)—H(1)—O(2) 162(5)°. Molecule **3** is planar: the angle between the C(1)—C(6) and C(8)C(10)O(1)O(2) planes is 2.4(3)°, the angle between the C(11)—C(16) and C(8)C(10)O(1)O(2) planes is 2.3(3)°, and the nitro group, unlike that in molecule **1**, is not shifted from the plane of the phenyl ring.

Molecule **3** exhibits an insignificant increase in the C(4)—O(5) and C(10)—C(11) bond lengths and a decrease in the C(1)—C(8) bond length compared to the corresponding bond lengths in molecule **1** (see Table 2). This can be attributed to a decrease in the influence of the nitro group on the π-system of the molecule. In fact, the Hammett constant for the nitro group in the *para*-position is 0.78, and that in the *meta*-position equals 0.70.[18] The decrease in π-conjugation in molecule **3** compared to molecule **1** is also manifested as the hypsochromic shift of the maxima of the absorption and fluorescence bands (see Table 3).

The structure of *p*-nitrobenzoylanisoylmethane crystals is presented by isolated molecules, which form a three-dimensional framework due to the van der Waals interaction. The distance between the planes of two adjacent parallel molecules of compound **1** is 3.57 Å, indicating that excimers can be formed.[19] However, the maxima of the bands in the absorption and fluorescence spectra of chloroformic solutions and crystals of compound **1** virtually coincide (see Table 3), which indicates, on the one hand, that the molecules in the ground state are not associated and, on the other hand, excimers are not formed. The absence of the interaction of molecules **1** in the crystalline state is explained, most likely, by the specificity of their mutual orientation: the donating (—C_6H_4OMe) and withdrawing (—$C_6H_4NO_2$) groups are arranged at a distance of 3.57 Å from the translationally identical groups. A resembling orientation of molecules is observed for compound **2**. However, in this case, the transition from crystals to a solution results in the 70-nm hypsochromic shift of the maximum of the fluorescence band (see Fig. 2, *b*, Table 3). Similar changes in the fluorescence characteristics on going from solutions to crystals have been found for dibenzoylmethanatoboron difluoride.[16] They are a result of the formation of excimers in concentrated solutions and crystals. However, in the case of compound **2**, its crystal structure does not allow one to explain the changes in the fluorescence characteristics observed on going from a solution to crystals by the formation of excimers because the adjacent molecules are not coplanar, *i.e.*, one of the main conditions of excimer formation is violated.[19]

Thus, the comparative study of the crystal structures and fluorescence characteristics of *p*- and *m*-nitrobenzoylanisoylmethanes and *p*-nitrobenzoylanisoylmethanatoboron difluoride shows that when the structures of HOMO and LUMO of the molecules under study are close, the geometric structure of the compounds has a considerable effect on the fluorescence intensity.

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