Fluorescence and photochemical properties of crystalline boron difluorides β-diketonato

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The fluorescence and photochemical properties of crystalline β-diketonatoboron difluorides (DBD) $RCOCHCOR^1BF_2$ were studied. These compounds are characterized by relatively high photochemical stability. The introduction of electron-donating groups into the aromatic α-substituent of the chelate ring increases and the introduction of electron-withdrawing groups decreases the fluorescence intensity of DBD. Anisoylbenzoylmethanotoboron difluoride was found to exhibit the highest fluorescence intensity. The substituents were shown to influence the relative arrangement of singlet and triplet $n\pi^*$ and $\pi\pi^*$ levels and luminescence properties of compounds.

Key words: boron, β-diketonates, luminescence.

In recent years, there has been a renewed interest in the photophysical and photochemical properties of β-diketonatoboron difluorides (DBD), promising for use in laser technology.[1,2] The photophysical properties of solutions of these compounds and the influence of the nature of the solvent on the spectral-luminescence and photophysical parameters of compounds were also described.[3,4]

Unlike complexes of d- and f-elements, DBD display substantial changes in photophysical characteristics on passing from the crystalline state to solutions.[1] Data on the photophysical and photochemical properties of crystalline DBD and their structure[5] are quite scarce. The present work reports fluorescence and photochemical properties of crystalline DBD of the composition $RCOCHCOR^1BF_2$, where $R = Me$, Ph, $C_{10}H_7$, p-$MeOC_6H_4$; $R^1 = Me$, Ph, $C_{10}H_7$, p-$MeOC_6H_4$, p-BrC_6H_4, m-$NO_2C_6H_4$, and p-$NO_2C_6H_4$ (Table 1).

Experimental

DBD were synthesized by a previously described procedure.[6] The purity of compounds was confirmed by the data of elemental analysis, IR spectroscopy, and GC/MS analysis. IR spectra of the samples (400—4000 cm^{-1}) were recorded on an Impact 400 instrument in KBr. UV spectra were measured on a Hitachi 220A instrument; the concentration of solutions was $1 \cdot 10^{-5}$ mol L^{-1}. Mass spectra were run on a gas chromatograph with a Hewlett Packard Hp 5890 II/5972 mass-selective detector. The volume of each sample was 1 μL with a flow ratio of 1 : 20; the rate of the carrier-gas (nitrogen) flow was 1 mL s^{-1}. The measurements were carried out under conditions

of full scanning of m/z from 50 to 410 (injector temperature 180 °C, detector temperature 280 °C, temperature programmed heating from 50 to 280 °C, heating rate 20 K min^{-1}, ionization energy 70 eV). The luminescence spectra of samples were recorded on an SDL-1 spectrometer. A DRSh-250 mercury lamp served as the source of excitation. The measurements were carried out at 300 K. Photolysis of compounds was performed by exposing the samples in a polyethylene matrix ($C = 10^{-3}$ mol L^{-1}) to the nonfiltered light of a DRT-250 mercury lamp. The light flux intensity ($\lambda_{excit} = 365$ nm) measured using a ferrioxalate actinometer was $2.75 \cdot 10^{15}$ quantum s^{-1}; the distance from the lamp to the sample was 20 cm.

Table 1. Position of the band maxima and relative intensities of fluorescence of crystalline β-diketonatoboron difluorides $(R^1COCHCOR^2)BF_2$ and maximum extinction coefficients of the absorption bands (solutions of compounds in chloroform)

Com-pound	R^1	R^2	λ_{fl}/nm	I_{fl}	$\varepsilon_{max} \cdot 10^{-4}$ (λ/nm)
1	Me	Me	470	0.001	1.6 (286)
2	Me	Ph	450	0.07	1.5 (330)
3	Me	$C_{10}H_7$	530	0.72	3.4 (344)
4	Me	p-$MeOC_6H_4$	505	0.23	4.1 (360)
5	Ph	Ph	530	1.0	1.8 (380)
6	Ph	m-$NO_2C_6H_4$	550	0.01	1.2 (358)
7	$C_{10}H_7$	Ph	530	1.16	1.9 (344)
8	$C_{10}H_7$	p-BrC_6H_4	575	0.26	7.2 (372)
9	$C_{10}H_7$	m-$NO_2C_6H_4$	520	0.1	2.4 (362)
10	$C_{10}H_7$	p-$NO_2C_6H_4$	565	0.09	2.5 (372)
11	p-$MeOC_6H_4$	Ph	560	3.94	1.2 (397)
12	p-$MeOC_6H_4$	p-BrC_6H_4	525	0.5	4.5 (404)
13	p-$MeOC_6H_4$	m-$NO_2C_6H_4$	545	0.02	1.6 (380)
14	p-$MeOC_6H_4$	p-$NO_2C_6H_4$	540	0.01	2.7 (386)

Results and Discussion

Figure 1 shows the variation of the fluorescence intensity of some DBD in a polyethylene matrix vs. the time of UV irradiation. The intensities of fluorescence of naphthaloylbenzoylacetonatoboron (3) and anisoylacetonatoboron (4) difluorides virtually do not decrease during irradiation with the nonfiltered light of a mercury lamp for 24 h. Benzoylacetonatoboron (2) and p-bromobenzoylanisoylmethanatoboron (12) difluorides exhibit lower photochemical stabilities.

According to the photoelectron spectroscopy data, the replacement of a hydrogen atom in Hacac (acetylacetone molecule) by a BF_2 group stabilizes two upper levels, π_3 and n, by 0.84 and 1.8 eV, respectively.[7] For benzoylacetone, stabilization of the two upper levels following the replacement of H by BF_2 is 0.45 and 0.3 eV, respectively.[7] The increase in the electron-donating ability of β-diketone observed on passing from compound 2 to compounds 3 and 4 together with the electron-withdrawing nature of the complexing group (BF_2) induce an increase in the degree of delocalization of the electron density of the π-system of the chelate ring and an enhancement of the photochemical stability of the molecule. Similar features have been observed in the studies of photochemical properties of lanthanide complexes.[8]

The positions of the band maxima and the relative fluorescence intensities found for crystalline DBD are presented in Table 1. The fluorescence spectra are shown in Figs. 2 and 3.

The highest fluorescence intensity in the series of compounds studied was found for anisoylbenzoylmethanatoboron difluoride (11). In the series of crystalline DBD, the intensity of fluorescence increases in the sequence acetylacetonate (1) < benzoylacetonate (2) < anisoylacetonate (4) < naphthaloylacetonate (3) <
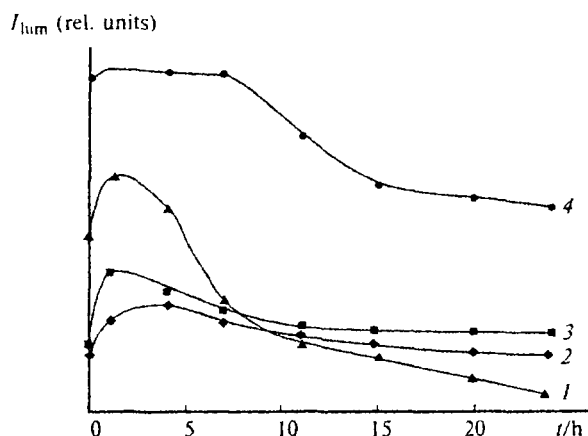

Fig. 1. Intensity of the luminescence of the DBD R¹COCHCOR vs the time of UV irradiation at 300 K. R¹, R = Me, Ph (*1*); $C_{10}H_7$, Ph (*2*); Me, p-MeOC₆H₄ (*3*); p-BrC₆H₄, p-MeOC₆H₄ (*4*).

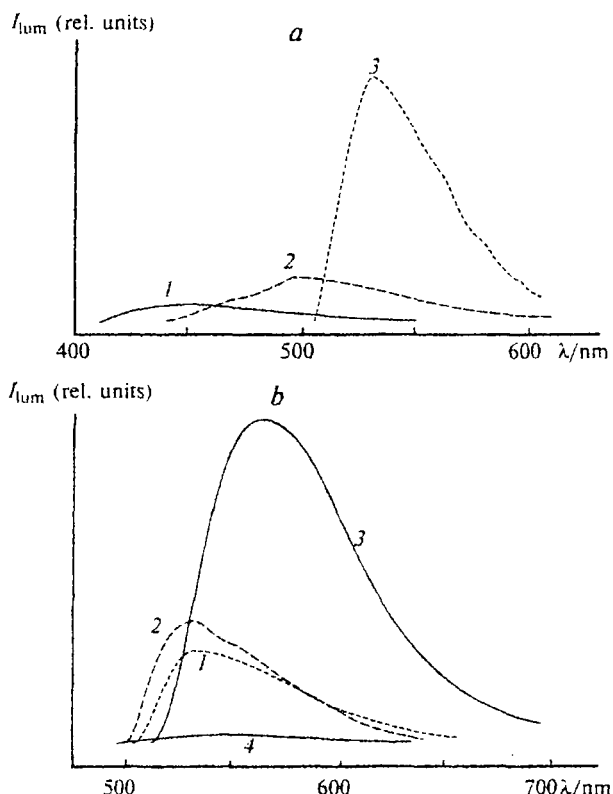**Fig. 2.** Luminescence spectra (λ_{exci} = 365 nm) of DBD. *a*, MeCOCHCOR, where R = Ph (*1*); $C_{10}H_7$, (*2*); p-MeOC₆H₄ (*3*); *b*, PhCOCHCOR, where R = Ph (*1*); $C_{10}H_7$ (*2*); p-MeOC₆H₄; m-NO₂C₆H₄ (*4*).

naphthaloylbenzoylmethanate (7), dibenzoylmethanate (5) < anisoylbenzoylmethanate (11).

The introduction of the electron-donating methoxy group into the benzene ring of the α-substituent in β-diketone results in a higher fluorescence intensity. On going from compound 2 to 4, the intensity increases 3-fold and on going from compound 5 to 11, it increases 4-fold (see Fig. 2).

Upon transition from compound 2 to compound 5 and from 4 to 11, the fluorescence intensity increases by a factor of more than 10, while on going from 3 to 7, it increases only 1.6-fold.

Meanwhile, the introduction of electron-withdrawing substituents (p-Br, p-NO₂, m-NO₂) into the benzene ring sharply decreases fluorescence (compounds 6, 8—10, and 12—14) (see Fig. 3).

It can be seen from the data given in Table 1 that replacement of an aliphatic α-substituent by an aromatic substituent is accompanied by a bathochromic shift of the fluorescence maximum. The greatest bathochromic shift of the fluorescence bands is observed for anisoylbenzoylmethanatoboron difluoride (λ_{lum} = 560 nm) and p-bromobenzoylanisoylmethanatoboron difluoride (λ_{lum} = 575 nm).

I_{lum} (rel. units)

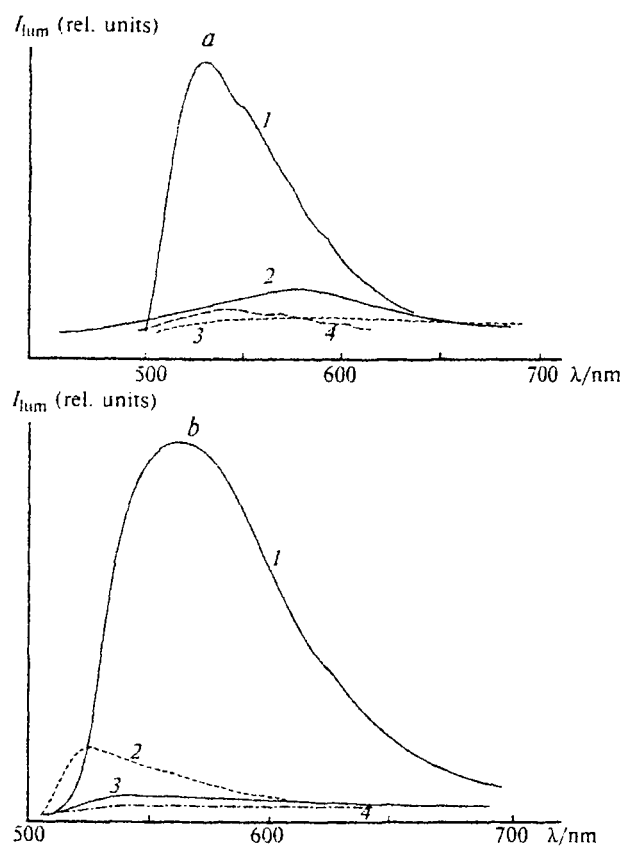I_{lum} (rel. units)

Fig. 3. Luminescence spectra (λ_{excit} = 365 nm) of DBD: _a_, $C_{10}H_7COCHCOC_6H_4R$. where R = H (_1_); _p_-Br, (_2_); _m_-NO_2 (_3_); _p_-NO_2 (_4_); _b_, _p_-MeOC$_6$H$_4$COCHCOC$_6$H$_4$R. where R = H (_1_); _p_-Br. (_2_); _m_-NO_2 (_3_); _p_-NO_2 (_4_).

In the series of compounds **2—4**, transition from benzoylacetonatoboron to naphthaloylacetonatoboron and introduction of a methoxy group into the benzene ring of benzoylacetonatoboron induce bathochromic shifts equal to 80 and 55 nm, respectively. On passing from compound **2** to compound **5** and from **4** to anisoylbenzoylmethanatoboron **11**, the fluorescence maximum undergoes substantial bathochromic shift; however, on going from **3** to **7**, the fluorescence maximum virtually does not shift.

The bathochromic shifts of the fluorescence maxima, observed upon introduction of substituents that extend the chain of conjugation of π-bonds into the phenyl group of dibenzoylmethanatoboron difluoride, points to a decrease in the energy gap between the highest occupied MO and the lowest unoccupied MO of the molecule.[9]

The fluorescence state can be deactivated as a result of the internal conversion (nonradiation processes), intercombinational conversion, or the transfer of energy to other molecules. The quantum yield of fluorescence is defined by the expression $\varphi_{fl} = \tau_{fl}/\tau_{fl}^0$, where τ_{fl} is the measured lifetime of the excited state; τ_{fl}^0 is the radiative

lifetime of the excited state. In addition, $\tau_{fl} = 1/\Sigma k_i$, where Σk_i is the sum of the rate constants for all processes resulting in the deactivation of excited states. The order of the radiative lifetime τ_{fl}^0 can be roughly estimated based on the experimental data on the molar extinction coefficients (ε) of the corresponding bands using the relation[9] $\tau_{fl}^0 = 10^{-4}/\varepsilon_{max}$. The ε_{max} values that we measured for the absorption bands of the complexes in question in a chloroform solution lie in the range $(1-7) \cdot 10^4$ L mol^{-1} cm^{-1} (see Table 1). The minimum ε value was found for compounds **6** and **11**, while the maximum value belongs to compound **8** (see Table 1). Thus, the τ_{fl}^0 values calculated for chloroform solutions of the complexes are close and vary from 1 to 13 ns (for **5**, $\tau_{fl}^0 = 5.5$ ns).

In the case of compound **5**, the quantum yield φ_{fl} measured experimentally in cyclohexane at ~20 °C is 0.046 and $\tau_{fl} = 0.14$ ns[10]; thus, $\tau_{fl}^0 = 3$ ns. Note that φ_{fl} depends appreciably on the solvent used, for example, this value for compound **5** in acetonitrile is 0.1.[10] The fluorescence properties of the complexes depend on the aggregative state. Indeed, on going from the crystalline state to solutions, fluorescence characteristics sharply change and the absorption maxima of all complexes undergo substantial (up to 100 nm) hypsochromic shifts. In addition, an increase in the concentration of a complex in a solution decreases the fluorescence intensity.

Geometric factors such as rigidity and planarity of the structure are significant for an increase in the yield of fluorescence. The structure of complex **2**, which has been solved, indicates that the benzene ring of the substituent is coplanar with the chelate ring.[5] The crystal structures of the enol forms of β-diketones incorporated in compounds **5**, **11**, and **13** are also known.[11] For dibenzoylmethane and 1-(_p_-methoxy)-3-(_m_-nitrophenyl)propane-1,3-dione, as for compound **2**, the benzene rings of the substituents are known to be coplanar with the chelate ring. In the case of 1-phenyl-3-(_p_-methoxyphenyl)propane-1,3-dione incorporated in compound **11** and exhibiting the greatest fluorescence intensity, the coplanarity is violated. As a consequence, the angle between the benzene ring containing the methoxy group and the chelate ring becomes equal to 26.5° and the angle between the planes of the α-substituents is 31°. Evidently, the electron-donating properties of substituents in β-diketone play a crucial role in the deactivation of the fluorescence state in the crystalline complexes studied.

The data presented in Table 1 show that the probability of the radiative S→S$_0$ transition depends only slightly on the introduction of aromatic substituents in the chelate ring. However, when the methyl groups in the β-positions (compound **1**) are replaced by aryl groups (phenyl, naphthyl, anisoyl), the energy of the S$_1$←S$_0$ electron transition substantially decreases and the fluorescence intensity increases by several orders of magnitude. Upon further introduction of a Br atom or an NO_2
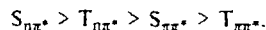
group into the aromatic substituent, the intensity of the fluorescence of the compounds sharply decreases.

The data obtained by photoelectron[7,12,13] and UV spectroscopy[14] help to analyze the mutual arrangement of the lower excited S_1 and T_1 levels of the $\pi\pi^*$ and $n\pi^*$ types, responsible for the spectral-luminescence characteristics of molecules.[9,15]

The structure of four upper occupied orbitals (π_3, n^-, n^+, π_3) in acetylacetonatoboron difluoride (compound 1) is similar to the structure of orbitals in the enol form of acetylacetone.[7] The gas-phase spectrum of acac in the enol form contains three bands; the low-intensity band with a maximum at 294 nm corresponds to the $\pi^*\leftarrow n$ transition and the two relatively intense bands at 263 and 176 nm are due to $\pi^*\leftarrow\pi$ transitions.[14] The only band displayed in the UV absorption spectrum of compound 1 has a maximum at 286 nm (see Table 1) and corresponds to the $\pi_4^*\leftarrow\pi_3$ transition (the weak band due to the $\pi^*\leftarrow n$ transition is masked by the above-mentioned transition and cannot be observed in the spectrum). In view of these facts and taking into account the low fluorescence intensity (see Table 1) and prolonged phosphorescence at 77 K ($\tau \approx 2$ s), compound 1 can be classified as a structure characterized by the arrangement of lower excited levels presented below.[9]

$$S_{n\pi^*} > S_{\pi\pi^*} > T_{n\pi^*} > T_{\pi\pi^*}$$
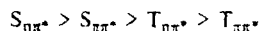
The data of photoelectron spectroscopy indicate[7,12] that the replacement of the β-methyl groups in β-diketonatoboron derivatives by aryl groups induces substantial changes in the composition of the HOMO. These changes are due to the interaction of π-orbitals of the substituent and the π_3 HOMO of β-diketone; the contribution of the substituent AO to the HOMO predominates over the contribution of the boron-containing ring. Thus, the predominant contribution of the orbitals of substituents to the HOMO for complexes with aromatic substituents and, correspondingly, the decrease in the contribution of n^- orbitals would result in the inversion of the $S_{\pi\pi^*}$ and $T_{n\pi^*}$ states with respect to their arrangement observed for compound 1. Thus the sequence of the lower excited energy levels acquires the pattern typical of the spectral-luminescence type of molecules

$$S_{n\pi^*} > T_{n\pi^*} > S_{\pi\pi^*} > T_{\pi\pi^*}.$$

Molecules of this type are known[9,15] to produce intense fluorescence.

Thus, the experimental data outlined above demonstrate that the introduction of electron-donating groups into the aromatic α-substituent in the chelate ring increases, while the introduction of electron-withdrawing groups markedly decreases, the intensity of fluorescence of crystalline β-diketonatoboron difluorides.

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