Reversible luminescence thermochromism of dibenzoyl(methanato)boron difluoride

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Reversible luminescence thermochromism of dibenzoyl(methanato)boron difluoride was found. A substantial hypsochromic shift of the luminescence band maximum (60 nm) with a temperature decrease from 300 to 77 K was observed, and the luminescence color changed from green to blue. A considerable decrease (by 0.386 Å) in the unit cell parameters along the *c* axis was detected by X-ray diffractometry when the temperature of the crystal decreased from 293 to 123 K. Shortening of the distances between the planes of adjacent molecules (stacking factor) weakens the interaction between the dimers and enhances the monomeric and excimeric luminescence.

Key words: dibenzoyl(methanato)boron difluoride, β-diketonates, fluorescence, luminescence thermochromism, stacking factor.

Development and synthesis of reversible luminescent thermochromes are urgent from both practical and theoretical standpoints.[1,2] One of the promising lines of search for new luminescent thermochromes is a study of molecular-organized organic systems, including dimers, trimers, and aggregates of conjugated molecules, whose supramolecular architecture produces different intermolecular interactions: dimeric (excimeric), interdimeric, and stacking interactions.[3,4]

Continuing our works on studying the interrelation of the structure and luminescence and photochemical properties of boron difluoride β-diketonates,[5—7] in this work we studied a change in the luminescence of dibenzoyl(methanato)boron difluoride (**1**) at different temperatures and revealed reversible luminescence thermochromism of this compound, namely, a substantial hypsochromic shift of the fluorescence band maximum (60 nm) and a change in the luminescence color from green to blue when the temperature decreases from 300 to 77 K.

Experimental

Compound **1** was synthesized according to a previously published procedure.[8] Crystals were prepared by recrystallization from an acetonitrile—toluene (1 : 1) mixture. Fluorescence spectra of solutions were obtained on a Shimadzu RF 5000 instrument. Luminescence spectra of crystalline compounds at 77—300 K were recorded on an SDL-1 spectrometer, using a DRSh-250 lamp as an excitation source and an UFS-6 filter (λ_{exc} = 365 nm). To measure a temperature dependence of the luminescence spectra, a sample was placed in a quartz Dewar flask above the liquid nitrogen surface. The temperature of the sample was measured by a platinum thermocouple. The X-ray diffraction study of compound **1** was carried out at 293, 203, and 123 K in a SMART-1000 CCD Bruker system using Mo-Kα radiation.

Results and Discussion

As can be seen from the data in Fig. 1, a decrease in the temperature of the crystal from 300 to 77 K produces a substantial hypsochromic shift of the fluorescence band maximum of compound **1** (60 nm). For a more detailed analysis of the evolution of the luminescence spectra with a temperature change, the spectra were deconvoluted by the Gaussian expansion using the Origin 6.1 program; the results of deconvolution are presented in Fig. 1.

It turned out that the fluorescence spectrum of compound **1** at each temperature consists of three components with maxima at 470, 500, and 560 nm, and only their relative intensity changes. When the temperature increases, the intensity of the short-wave components (470 and 500 nm) decreases and the contribution of the long-wave component with a maximum at 560 nm increases. The resulting spectrum at 300 K represents a broad nonsymmetric band with a maximum at 530 nm (see Fig. 1).

To refine the nature of the components of the fluorescence spectra of compound **1**, we compared the spectra of the crystals and solutions at different concentrations. Boron difluoride β-diketonates are characterized by both the fluorescence of single molecules[9] (in dilute solutions) and

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 1032—1034, April, 2005.

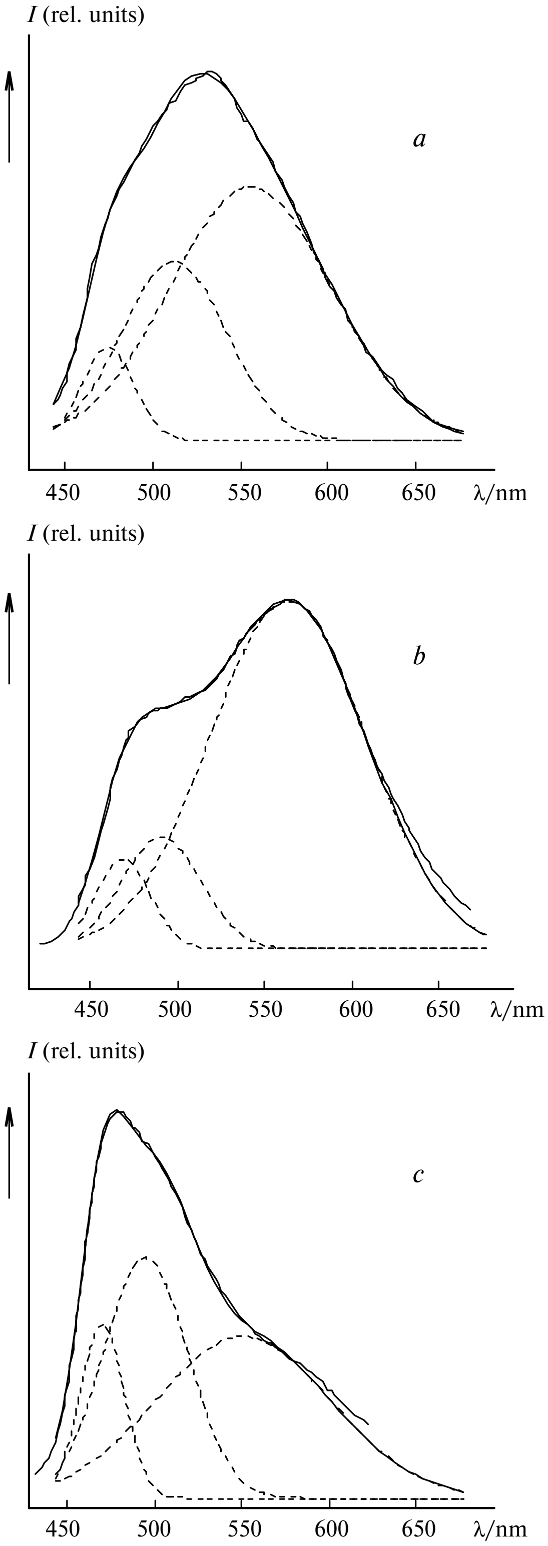

Fig. 1. Fluorescence spectra of crystals **1** (solid lines) at 300 (*a*), 120 (*b*), and 77 K (*c*) and the result of their Gaussian deconvolution (dotted lines).

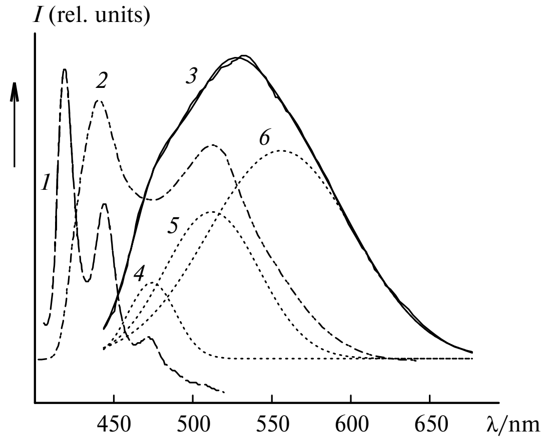

Fig. 2. Fluorescence spectra of compound **1**: *1*, solution in isopropyl alcohol at 77 K, $C = 10^{-4}$ mol L^{-1}; *2*, solution in chloroform at 300 K, C = 0.9 mol L^{-1}; *3*, crystals at 300 K; *4*, *5*, and *6*, result of deconvolution of the fluorescence spectrum to components.

excimers[5,10] (in concentrated solutions). As can be seen in Fig. 2, the band with a maximum at 500 nm is due to excimer fluorescence in concentrated solutions of dibenzoyl methanate **1**.[5] The band with a maximum at 470 nm coincides with the long-wave band in the fluorescence spectrum of a solution with a low concentration of compound **1**. According to published data,[9] the absence of two other fluorescence bands of single molecules (420 and 444 nm) from the spectrum of the crystals can be due to the fact that solutions of **1** contain rotamers with different positions of the Ph rings relatively to the plane of the diketonate cycle (Scheme 1).

Rotamer formation becomes impossible on going to crystal **1**, because the fluorescence spectrum of the monomers is transformed into one band with a maximum at 470 nm, for which the contribution of torsional vibrations is insubstantial.[9] Thus, the first band in the fluorescence spectrum of crystals **1** (470 nm) can be assigned to fluorescence of the single molecules, the second band (500 nm) can be attributed to fluorescence of the excimers themselves, and the third band (560 nm) is caused by fluorescence of interdimeric associates, which, as has been shown previously,[4,6] is characteristic of compounds consisting of infinite piles of mutually intersecting molecules.

Thus, the luminescence thermochromism of compound **1** can be related to a considerable decrease in the contribution of the interdimeric interaction to the overall fluorescence spectrum and growth of the fluorescence intensity of the monomers and excimers with a temperature decrease.

We have earlier[5] determined the crystal structure of compound **1**. The molecules in crystal are arranged as infinite stacks parallel to the *c* axis. Two types of intersecting molecules alternate within the stacks of crystals **1**. For the first type, the Ph rings of two adjacent molecules overlap, and the second case is the overlap of the diketonate and phenyl rings of the adjacent molecules.[5] As

Scheme 1

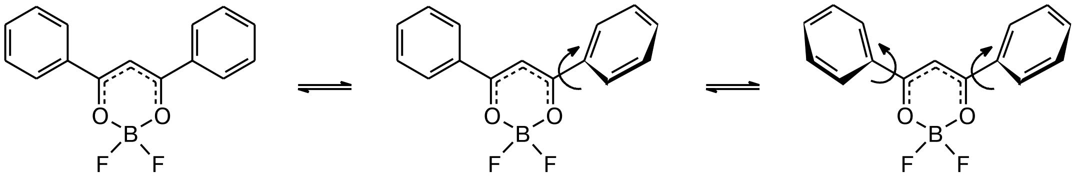

Table 1. Unit cell parameters for **1** at different temperatures

T/K	*a*	*b*	*c*	α	β	γ
	Å			deg		
296	13.8049	13.9926	14.1262	90.000	107.318	90.000
203	13.7773	13.9324	13.8976	90.000	107.241	90.000
123	13.7720	13.9015	13.7457	90.000	107.271	90.000

a whole, the architecture of molecular crystals **1** favors the appearance of stacking interaction.

The unit cell parameters of crystal **1** were measured at different temperatures (Table 1). As the temperature decreases, the *a* and *b* parameters reflect their natural decrease in directions close to the plane of molecules **1**, whereas a considerable decrease in the parameter toward the *c* axis (0.386 Å) reflects a substantial decrease in the distances between the planes of adjacent molecules in the piles.

A decrease in the distance between the adjacent molecules by ~0.1 Å with a temperature decrease from 293 to 123 K enhances the stacking effect. It should be taken into account that in the ground state repulsion forces, which are approximately proportional to the surface area of overlap of the π-systems of the adjacent molecules, are among the most important components for the π—π-electron stacking interaction.[10] When the intermolecular distances decrease, attraction between the excited excimer-forming molecules enhances, on the one hand, while on the other hand, repulsion between the molecules in the ground state increases.[11,12] The result of this change in the intermolecular interaction is the decrease in the interdimeric interaction and enhancement of fluorescence of the monomers and excimers with the temperature decrease.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 04-03-33155).

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Received September 1, 2004;
in revised form March 11, 2005