Crystal Structure and Excimer Fluorescence of Some Benzoylacetonatoboron Difluorides: Stacking Factor

**A. G. Mirochnik,[1] B. V. Bukvetskii,[1] E. V. Gukhman,[1, 2] and V. E. Karasev[1]**

The comparative study of the crystal structures of benzoylacetonato- (**1**), *p*-toluylacetonato- (**2**) and *p*-ethylbenzoylacetonatoboron (**3**) difluoride was carried out. Correlation of the luminescence properties of the complexes **1–3** and their crystal structures was revealed. The excimer formation in these compounds occurred the most efficiently for the complexes **1** characterized by the formation of stacks of molecules, unlike the complex **3**, where individual dimers behaved as excimer-forming centers. The maximal fluorescence intensity was observed for the complex **2**, which had the highest structural ordering.

INTRODUCTION

To date, the photophysical and photochemical behavior of diluted solutions of some β-diketonatoboron difluorides has been studied extensively [1–5]. However, only a few works are devoted to the correlation of the crystal and molecular structures of β-diketonatoboron difluorides with their spectral properties [6–8].

The present work describes the results of the fluorescence and photochemical properties studies of benzoylacetonatoboron difluorides with alkyl substitutes in the phenyl ring (Scheme 1) and their crystal structures.
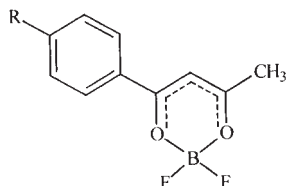
Scheme 1. Chemical structures of the compounds **1–3**. **1**: R = H; **2**: R = CH$_3$; **3**: R = C$_2$H$_5$.

[1] Institute of Chemistry, Far-Eastern Branch of the Russian Academy of Sciences. 159 prosp. 100-letiya Vladivostoka, 690022 Vladivostok, Russian Federation.
[2] To whom correspondence should be addressed. Fax: 007(4232)311 889. E-mail: gev@ich.dvo.ru

EXPERIMENTAL

Benzoylacetonatoboron difluoride (**1**) was prepared and purified according to ref. [9]. *p*-Toluylacetonatoboron difluoride (**2**) and *p*-ethylbenzoylacetonatoboron difluoride (**3**) were prepared and purified according to reference [10]. Crystals of compounds **2** and **3** were prepared by crystallization from a butanol-1–acetonitrile (3:1) mixture. Concentrations of the compounds **1–3** solutions in chloroform are shown in Table I. Luminescence end excitation spectra of the crystal compounds were registered at the temperatures 77 and 300 K on the device constructed on the basis of an SDL-1 spectrometer (Lomo, Russia) (λ$_{ex}$ = 365 nm). The fluorescence spectra of the solutions were recorded on a JASCO FP-550 spectrometer (Japan) (λ$_{ex}$ = 365 nm). The complete X-ray study was performed on a SMART-1000 CCD instrument (Bruker, Madison, WI) using Mo Kα radiation. Accumulation of the data, their correction, refinement of the unit cell parameters, and recalculation of the integral intensities into the structural amplitude modules were made according to known programs [11, 12]. The crystal structure was solved by the direct method with the following refinement of the positional and thermal parameters in the anisotropic approximation for all the nonhydrogen atoms by known

Table I. Spectral Properties of **1–3**

Compound	Concentration (mol·l^{-1})			Fluorescence of solutions (λ_{max}/nm)			Fluorescence of crystals			
							300 K		77 K	
	C_1	C_2	C_3	C_1	C_2	C_3	λ_{fl} (nm)	$I_{real}{}^h$	λ_{fl} (nm)	$I_{real}{}^h$
1	0.2	0.016	0.0013	475	400, 423, 480	400[a], 423	450	1	461	1
2	0.045	0.018	0.0036	400, 443	395, 440[a]	400	444, 494[c]	2	450, 485, 501	1.45
3	0.036	0.0033	0.00027	426[a], 466	426, 472	426, 475[a]	475	1.3	453	0.48

[a] The wing.
[b] The integral intensity of **1** at the respective temperature is used as the fluorescence intensity unit.
[c] The decomposition of the fluorescence spectrum into its subcomponents was carried out by means of MicroCal Origin (Version 5.0).

programs. Although the hydrogen atom positions were determined by the electron density syntheses, in further study, the data calculated and refined by means of the ridering model were used.

The main crystal parameters of the samples, the X-ray diffraction data, and the structural model refinement details carried out by the least-squares method are given in Table II.

RESULTS AND DISCUSSION

The fluorescence spectra of all crystal compounds and their chloroform solutions of various concentrations were recorded at 77 and 300 K (Table I, Figs. 1–3).

Table II. Summary of Crystallographic Data for **2** and **3**

	2	3
Formula	$C_{11}H_{11}BF_2O_2$	$C_{12}H_{13}BF_2O_2$
M	224.01	237.03
Crystal system	Orthorhombic	Monoclinic
Space group	$Pca2_1$	$C2/c$
a (Å)	22.673 (3)	19.462 (3)
b (Å)	6.8267 (9)	12.179 (2)
c (Å)	7.1022 (9)	13.386 (2)
β (°)		129.813 (2)
V (Å^3)	1099.3 (3)	2437.2 (5)
Z	4	8
T (K)	296 (2)	296 (2)
μ(mm^{-1})	0.112	0.105
Unique reflections collected	4734	3281
Observed data [$I > 2\sigma(I)$]	1314 ($R_{int} = 0.0581$)	1009 ($R_{int} = 0.0229$)
Data/parameters	1314/148	1009/157
Final R1, wR2 indices [$I > 2\sigma(I)$]	0.0375, 0.0743	0.0512, 0.1536

Refinement method: Full-matrix least squares on F^2. Graphite-monochromatizer Mo Kα radiation, $\lambda = 0.71073$ Å.

The intensity of the fluorescence band in the short-wave part of the spectrum reduces with the increase of **1–3** concentration in the solution and, simultaneously, a broad structureless fluorescence band appears and increases in the long-wave region (Fig. 1). Similar changes can be observed in the fluorescence spectra with the concentration increase when excimer formation takes place [8,13]. The UV spectra of the crystal complex **1** and its diluted solution measured in ref. [6] have similar maxima of the absorption bands that excludes a possibility of aggregation of molecules in the ground state and enables one to assign a long-wave band in the fluorescence spectra of the concentrated solutions to the excimer fluorescence and a short-wave band to the monomer fluorescence, respectively. A similar situation (existence of short-wave monomer fluorescence and long-wave eximer fluorescence) is observed for **2** and **3** as well. As seen from Table I data, the maximums of monomer fluorescence positions for solutions with concentrations C_2 and C_3 are close to each other. Similarly, maximum values of the eximer fluorescence bands **1–3** are close for solu-
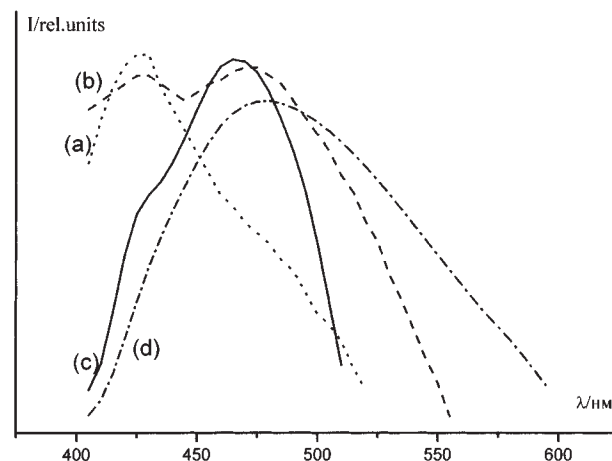

Fig. 1. Fluorescence spectra of **3** solutions in chloroform [$C = 2.7 \times 10^{-4}$ M (a): 3.3×10^{-3} M (b); 3.6×10^{-2} M (c)] and its crystals (d).
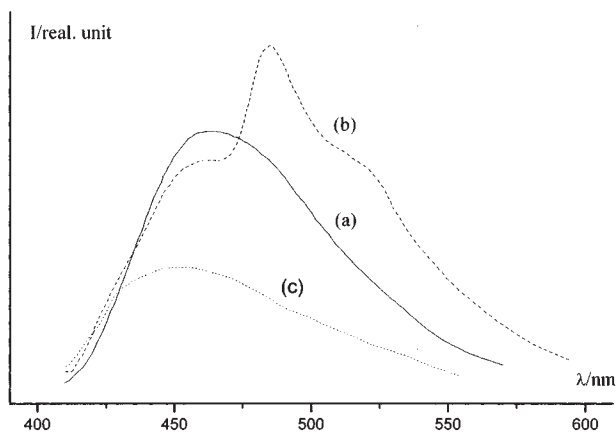
Fig. 2. Fluorescence spectra of the compounds: **1** (a), **2** (b), **3** (c) at 77 K.

tions of increased concentrations C_2 and C_1 and their crystals at room temperature (Table I). Thus, the analysis of spectral data of **1–3** (Table I) indicates the closeness of the energetic characteristics of the eximers formed.

Substitutes in the phenyl ring of boron difluoride alkylbenzoylacetonates do not have a substantial impact on the molecule π-system that is reflected in a closeness of the solution's fluorescence maximums (Table I). The steric factor of these substitutes is here far more substantial that is displayed in different crystalline structures of **1–3** and, as a result, a difference in their fluorescence spectra is observed, especially at 77 K.

The X-ray data are an additional confirmation of the excimer formation in **1–3**. The efficiency of the excimer formation depends upon that of the π–π interaction of the nearest molecules and peculiarities of the molecule packing in the crystal [14,15].
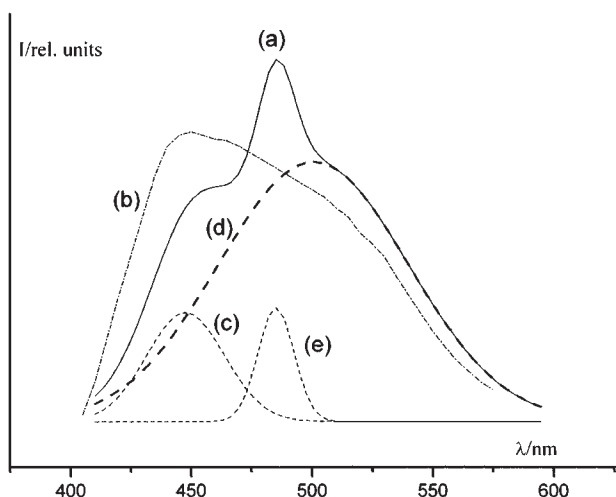

Fig. 3. Fluorescence spectra of **2** at 77 K (a) and at 300 K (b). The results of the decomposition of the spectrum at 77 K into the subcomponents (c)–(e).

Comparison of the molecular structure of **1** [16] and our data for **2** and **3** showed that the geometric parameters of the respective bonds in all the compounds had similar values. It shows that the peculiarities of the crystal structure substantially influence the fluorescence properties.

The formation of dimers where the molecules are arranged in such a way that the phenyl ring of one molecule is over the chelate cycle of another one is a common feature of the crystal structures **1–3** (Figs. 4 and 5). Unlike the complex **1**, in which a reciprocal overlap of the phenyl and chelate ring of the nearest molecules takes place, the absence of such overlap in **2** and **3** (Figs. 4b and 5b) virtually excludes a possibility of interaction of the phenyl and chelate ring π-systems in the ground state.

According to ref. [7,16], the molecules in **1** are packed as stacks parallel to the C-axis with the intermolecular distance 3.44 Å. Inside the stack, the molecules are multiplied by the screw-axis 2_1. The nearest stacks are reciprocally perpendicular.

The crystals of **2** are rhombic; their unit cell contains four coplanar molecules arranged in pairs; moreover, along the C-axis, the molecules are packed as stacks parallel to the A-axis with the intermolecular distance 3.54 Å (Fig. 4a). Inside the stack, the molecules are multiplied by the slide-reflection plane (Fig. 4b).

The crystals of **3** are monoclinic. Their unit cell contains eight molecules arranged on four levels (Fig. 5a). The molecules of the first and second levels are parallel and form a layer consisting of dimers with the intermolecular distance 3.67 Å (Fig. 5a). In these dimers, the phenyl ring of one molecule is directed to the chelate ring of another one (Fig. 5b). The same picture is observed for the third and fourth levels. Inside the layer the dimers are situated as a T, with the angle 70° between; the layers are displaced in such a way that the dimers arranged one over another are at the angle 70°. Moreover, the dimers of the two nearest layers are not parallel (the angle between the normals directed to the molecule center is 175°) (Fig. 5c).

Thus, the analysis of the crystal structure of **1** and **2** shows that the formation of stacks of molecules is typical for all of these complexes, but in **2** all the stacks are parallel, whereas in **1**, the neighboring ones are perpendicular. As for **3**, the absence of molecular stacks is its typical feature (Fig. 5c), unlike **1** and **2**, and only the dimers consisting of the molecules from the first and second levels are the excimer-forming centers (Fig. 5b). Analysis of the crystal parameters shows that the shortest distances between nearest molecules of one layer in the structures **1–3** differ slightly (2.57 Å for **1**, 2.60 Å for **2**, 2.64 Å for **3**). The reciprocal orientation of the molecular stacks exerts the main influence upon
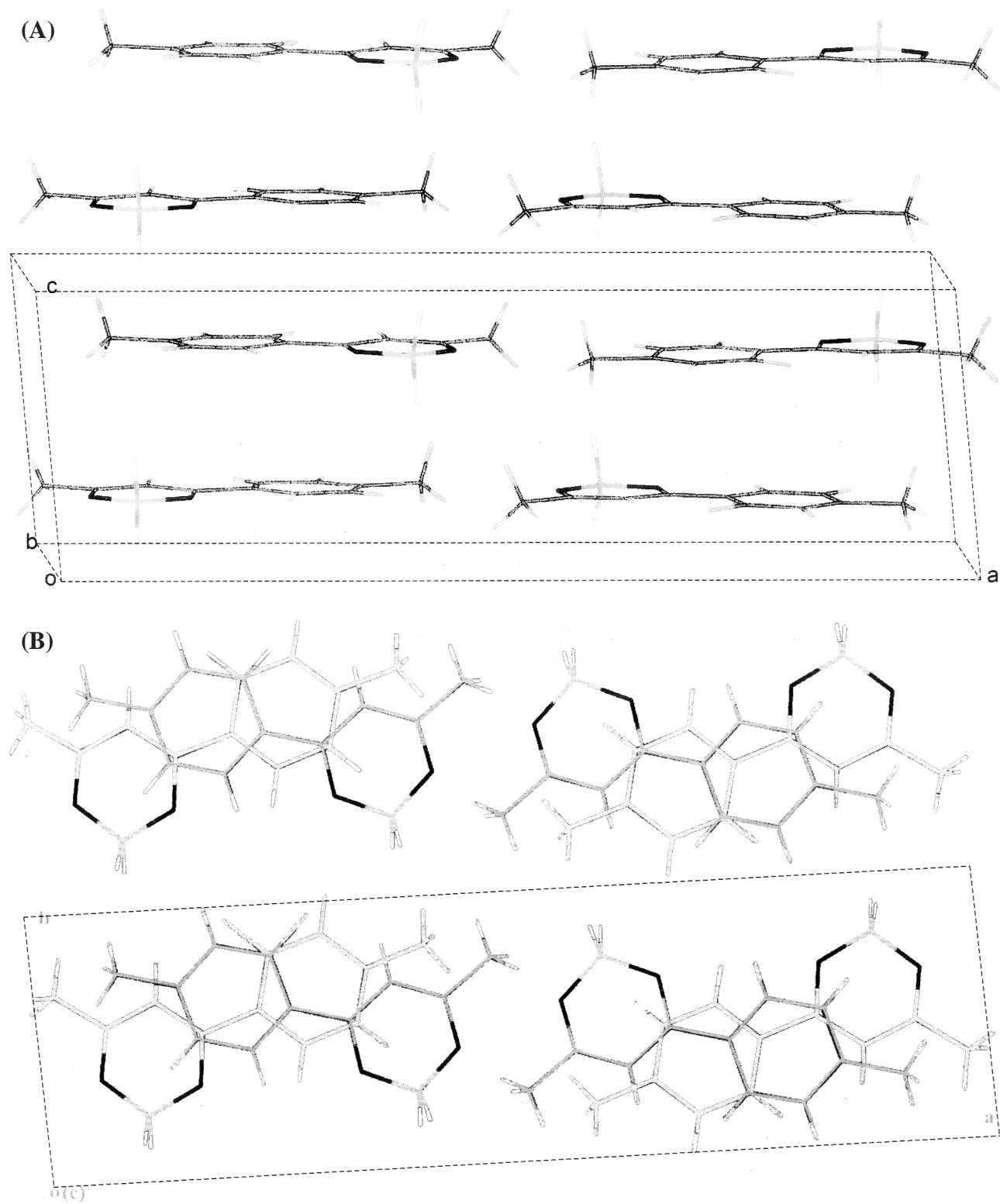
(A)

(B)

Fig. 4. Crystal structure of **2**: (A) the structure viewed along **b**; (B) the structure viewed along **c**.

(A)

layer of dimer

layer of dimer

level 4

level 3

level 2

level 1

b
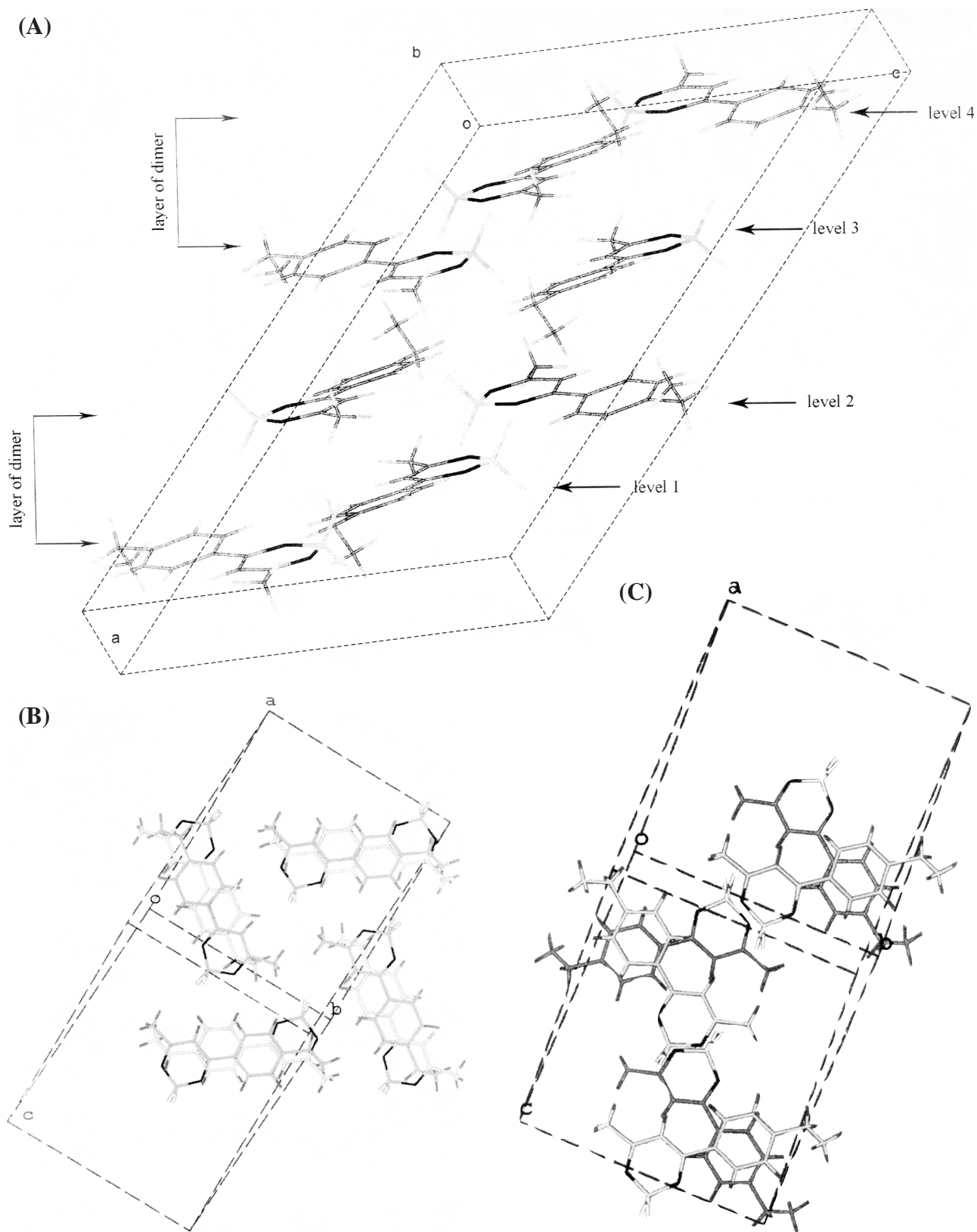
o

c

a

(B)

a

o

b

c

(C)

a

o

c

Fig. 5. Crystal structure of **3**: (A) crystal cell; (B) dimers layer; (C) the nearest levels of the molecules from different dimers layers.

efficiency of interaction among them: the parallel orientation of the stacks in **2** promotes more effective interdimer interaction.

Hence, the excimer formation in the series **1–3** must be the most efficient in **1** and **2** for which the presence of the stacks of the excimer-forming molecules is characteristic. Indeed, the crystals of **3** have a lower luminescence intensity as compared to those of **1** and **2** (Table I). The fluorescence spectra of the crystals **1** and **3** at 300 K are broad structureless bonds. At the same time, one can distinguish the two components with the maxima at 447 and 500 nm in the spectrum of **2**. Despite of close values of the fluorescence band maximums of the eximers **1–3** (Table I), the structures of the crystals' fluorescence spectra are not identical.

The analysis of the fluorescence spectra structure at low temperatures is an additional confirmation of the crystal structure effect upon excimer formation into the crystals.

The temperature decreasing to 77 K results in insignificant shift of the fluorescence spectrum maxima for **1** and **3**, whereas for **2**, structurization of the fluorescence spectrum takes place and the new band with the maximum at 485 nm appears (Fig. 3, Table I). The shortwave maximum in the fluorescence spectrum of **2** at 77 K and 300 K coincides with the maximum of that for the concentrated solution **2** (447 nm) (Table I) that enables one to assign this band to the excimer fluorescence.

It is interesting to determine the reason of appearance of the two additional bands in the luminescence spectrum of **2**. In view of this, the results published in reference [17] are worth mentioning. The authors studied the excimer formation in pyren crystals at low temperatures. The two bands in the fluorescence spectra were assigned to two types of interaction: the shortwave bond was assigned to the usual excimer fluorescence of pyren dimer, and the longwave band was assigned to an additional interdimer interaction. Similarly, the fluorescence peculiarities of **2** can be explained by its crystal structure. It was shown that **2** has the largest structural regularity in the series of the complexes studied (the presence of the parallel molecule stacks). This peculiarity can promote an additional interdimer interaction already at room temperature (the band at 500 nm). The decreasing temperature intensifies this interdimer interaction and results in the new band (485 nm).

CONCLUSIONS

Thus, our comparative study of the crystal structure of benzoylacetonato- (**1**), p-toluylacetonato- (**2**), and p-eth-

ylbenzoylacetonatoboron (**3**) difluoride and their luminescence properties showed the correlation between the spectral features of these complexes and the peculiarities of their crystal structure. The excimer formation in the series **1–3** is the most efficient in **1** for which the formation of stacks of the is typical, unlike the complex **3**, in which individual dimers behaved as the excimer-forming centers. The maximal fluorescence intensity was observed for the complex **2**, which had the largest structural ordering.

REFERENCES

1. Y. L. Chow, S.-S. Wang, Z.-L. Liu, V. Wintgens, P. Valat, and J. Kossanyi (1994) Photochemistry and photophysics of dibenzoylmetanatoboron difluoride with cyclic dienes. Effect of excited state molecular association in benzenoid solvents. *New J. Chem.* **18**(8–9), 923–936.
2. Y. L. Chow, S. P. Wu, and X. Ouyang (1994) Potocycloaddition of phenantrene with acatylacetonateboron difluoride: exciplex reactions. *J. Org. Chem.* **59**(2), 421–428.
3. Y. L. Chow and X. Ouyang (1991) The photoaddition of 1.3 diketonatoboron with benzene derivatives. *Can. J. Chem.* **69**, 423–431.
4. P. Valat, V. Wintgens, Y. L. Chow, and J. Kossanyi (1995) Unusually strong emission from an exciplex formed between beezonoid solvents and dibenzoylmetanatoboron difluoride. Formation of a triplex. *Can. J. Chem.* **73**, 1902–1913.
5. Y. L. Chow, C. I. Johansson, and Z.-L. Liu (1996) Ground- and excited state electron donor-acceptor (EDA) complexees from dibenzoylmetanatoboron difluoride and substituted benzenes: their relation to the reaction mechanism. *J. Phys. Chem.* **100**(32), 13381–13385.
6. G. Gortlitz, H. Hartmann, J. Kossanyi, P. Valat, and V. Wintgens (1998) Spectroscopic anomalies in the 4-aryl-2,2-difluoro-6-methyl-1,3,2-dioxaborine series. *Ber. Busenges. Phys. Chem.* **102**(10), 1449–1458.
7. Y. Dromzee, J. Kossanyi, V. Wintgens, P. Valat, H. Hartmann, and G. Gortlitz (1997) Crystal and molecular structure of unstructure of unsubstitutied and p-methoxy-substitutied acetylbenzoyl methanatoboron difluoride. *Z. Kristallogr.* **212**, 372–376.
8. A. G. Mirochnik, B. V. Bukvetskii, E. V. Gukhman, and V. E. Karasev (2001) Crystal structure and excimer fluorescence of dibenozoylmetanatoboron difluoride. *Russ. Chem. Bull.* **50**, 1612–1615.
9. V. E. Karasev, O. A. Korotkikh (1986) Spectral-luminescence properties of F_2B-β-diketonates. *Russ. J. Inorg. Chem.* **31**(4), 869–872.
10. V. A. Reutov and E. V. Gukhman (1999) Boron difluoride-beta-diketonates: I. Methods for preparing boron difluoride chelates with beta dicarbonyl compounds. *Russ. J. Gen. Chem.* **69**(10), 1603–1607.
11. Bruker (1998) *SMART and SAINT-Plus, Version 5.0. Data Collection and Processing Software for the SMART System.* Bruker AXS Inc., Madison, WI.
12. Sheldrick G. M. (1998) *SHELXTL/PC, Version 5.10. An Integrated System for Solving. Refining and Displaying Crystal Structures from Diffraction Data.* Bruker AXS Inc., Madison, WI.
13. M. Gordon and W. R. Ware (Eds.) (1975) *The Exciplex,* Academic Press, New York. 372 pp.
14. M. Pope and C. E. Swenberg (1982) *Electronic Processes in Organic Crystals,* Clarendon Press. Oxford.
15. N. N. Barashkov, T. V. Sakhno, R. N. Nurmukhametov, and O. A. Khakhel (1993) *Russ. Chem. Rev.* **62**(6), 579–593.
16. A. W. Hanson and E. W. Macaulay (1972) The crystal structure of benzoylacetonato boron difluoride. *Acta Crist.* **28**(1), 1961–1967.
17. H. Dauber, V. I. Yudson, and P. Reineker (1997) Excimer formation in pyrene crystals. *J. Lumin.* **72–74**, 909–911.