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The First Mesogenic Derivative of Boron Difluoride β-Diketonate

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Abstract—Boron difluoride β-diketonate exhibiting liquid crystalline as well as photoluminescence properties was prepared for the first time. It is the promising material for creating supramolecular organized luminescent media.

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An interest to investigation of photophysical and photochemical properties of the boron difluoride β-diketonate derivatives permanently increases because they exhibit high luminescence in the visible range of spectrum [1–5]. Because of their luminescence property these compounds can be used in luminescent analysis as the components of the light-emitting materials [6, 7]. Obtaining the compounds capable of luminesce in the yelloworange and the red range is particularly important [8, 9].

Boron difluoride β-diketonates were obtained rather long ago (in 1924) and the methods of their synthesis are considerably well known and systematized [10, 11]. Some compounds were the objects of X-ray studies [2, 3], and their luminescent properties were investigated. It was shown that their luminescence intensity depends on the geometry and electronic structure of the complexes [12]. It was noted that the mechanisms of luminescence in solution differs from that in the crystalline state [13].

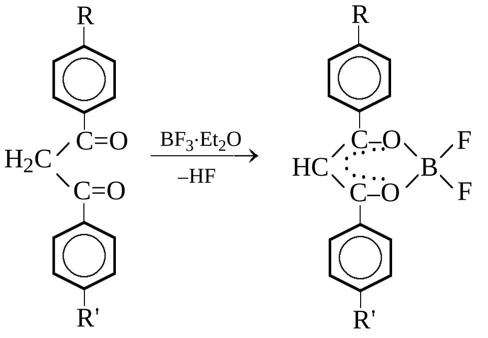
With the purpose of broadening the class of compounds exhibiting intense luminescence we prepared the first derivative of boron difluoride diketonate, boron difluoride 1-(4-dodecyloxyphenyl)-3-(4-tetradecyloxyphenyl)-propan-1,3-dionate, possessing liquid crystal properties. Presence of mezogenic properties is a new fact for the compounds of this class, permitting to approach to the solution of the problem of obtaining of supramolecular organized media necessary for creating the materials for the photonic devices [14, 15].

On the basis of the substances combining both liquid crystal and luminescence properties it may be possible to create defectless optic nanomaterials with monoaxially oriented molecules of a mesogen, exibiting highly efficient luminescence. We have reported previously on the preparation of the liquid crystalline complexes of lanthanoids forming ordered supramolecularly organized media and exhibiting lineary polarized luminescence [16, 17]. On an example of a series of compounds it was shown that inclusion of electron-donating groups to the aromatic α-substituent of the chelate ring and elongation of the conjugation chain leads to increase in the intensity of luminescence [1, 8]. Presence of aromatic groups and fluorine atoms in the molecule of luminophore also improves the brightness of radiation [18, 19].

In the present work we describe syntheses of nonmezogenic and liquid crystalline boron difluoride β-diketonates and compare their luminescent properties. Nonmezogenic dibenzoylmethane **I** (mp 79°C) and 1-(4-dodecyloxyphenyl)-3-(4-tetradecyloxyphenyl)-propan-1,3-dione **IIa** (mp 89°C) were chosen as the ligands.

β-Diketone with the long alkyl substituents was obtained by the multistage synthesis reported in [20].

For the investigation of the relationship between the structure and the physicochemical properties the complex of boron difluoride with dibenzoylmethane was prepared [scheme (1)]. Composition and structure of the obtained compounds were established by means of the elemental analysis, IR and ^1H NMR spectroscopy, and by the consistence of the physicochemical constants of compounds **Ia** and **Ib** with the previously reported data. The products obtained are stable in air and in solutions. Their chemical stability (remaining unchanged of the quasiaromatic ring in the reactions of electrophilic and nucleophilic substitution) was described in the preliminary report [11].

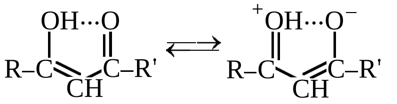


(1)

Ia, IIa **Ib, IIb**

R = R' = H (**I**); R = $C_{12}H_{25}O$, R' = $C_{14}H_{29}O$ (**II**).

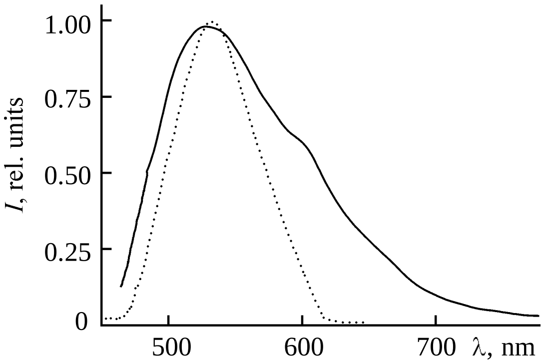
IR spectra of chelate complexes show a shift of the bands of stretching vibrations of C=C and C=O bonds (1592 and 1538 cm^{-1} respectively) as compared to the ligand (1582 cm^{-1} for C=C bond and 1600 cm^{-1} for C=O bond). Though it is known that the C=O bond in the ligand is weakened due to the resonance of the structures [21] [scheme (2)], the complex formation with boron difluoride leads to even more significant weakening of this bond arising from the withdraw of electronic density from the chelate ring by the fluorine atoms, and to decrease of the vibration frequency.



(2)

In the ^1H NMR spectrum the downfield shift of the signal of CH proton by 0.39 ppm and 0.40 ppm for compounds **Ib** and **IIb** respectively as compared to the ligands is observed, what is also explained by the effect of electronegative fluorine atoms on the electron density of the quasiaromatic cycle of the complex [22].

The liquid crystalline properties of compound **IIb** were investigated by means of the optic polythermal polarization microscopy. With the complex of substituted boron fluoride β-diketonate we have demonstrated formation of thermotropic smectic *A* phase $Cr92S_A129I$ (where *Cr* is the crystalline phase, S_A is the smectic *A* mesophase and *I* is the isotropic phase) which was identified by the characteristic fan-like texture. In the course of several cycles of heating and cooling and also at the prolonged keeping of the sample in the mesophase state its mesogenic structure and its parameters remained unchanged.



Normalized photoluminescent spectra of the polycrystalline samples **Ib** (dotted line) and **IIb** (continuous line) at room temperature.

UV spectra (in chloroform) of the obtained compounds contain absorption bands in the range 265–400 nm related to π–π* transitions in the chelate ring. The figure shows normalized photoluminescence spectra of the samples **Ib** and **IIb** in the polycrystalline state at room temperature. The maximum point of photoluminesce band of the liquid crystalline complex **IIb** (530 nm) corresponds to the maximum point of the band of the unsubstituted complex **IIb**. Its spectrum was published previously [2].

Hence, boron difluoride β-diketonate posessing the liquid crystalline as well as the photoluminescent properties was prepared for the first time. The intensity of radiation of the liquid crystalline sample has the same order as that of the crystalline one.

EXPERIMENTAL

The textures and the phase transfer temperatures were obtained on a Boetius polarizational microscope equipped with the temperature block controlled by a personal computer. The accuracy of the temperature measurements is 0.1°C. The IR spectra were registered on a Specord IR-75 spectrometer in vaseline oil. The ^1H NMR spectra were taken on a Bruker Avance 400 spectrometer in $CDCl_3$ against TMS. The UV spectra were measured in chloroform at the concentrations $1.5–3 \times 10^{-4}$ mol l^{-1} on a Specord UV-Vis spectrophotometer. Photoluminiscence spectra of the samples under investigation were obtained on a polyfunctional automatized optical spectrometer constructed on a base of KSVU-23 instrument. Pulse nitrogen laser LGI-21 (wavelength 337 nm, pulse duration 10 ns, pulse frequency 50 Hz) was used as a source for excitation. A FEU-100 photomultiplier was used as a photodetector. Photoluminescence spectra were registered3 mcs after the exciting impulse. The measurenents were carried out at room temperature.

The complex of boron difluoride with dibenzoylmethane was obtained as follows. Equivalent amount of the boron trifluoride etherate was added dropwise to the stirred hot solution of the ligand in toluene. The reaction mixture was boiled for 5–10 min and then cooled to room temperature. The precipitate obtained was filtered off. Reaction products were yellow powders well soluble in most organic solvents.

Boron difluoride 1-(4-dodecyloxyphenyl)-3-(4-tetradecyloxyphenyl)-propan-1,3-dionate (IIb). 1-(4-Dodecyloxyphenyl)-3-(4-tetradecyloxyphenyl)-propan-1,3-dione, 0.09 g, was added with stirring to 5 ml of absolute toluene, and 0.02 ml of boron difluoride etherate was added dropwise with stirring. Resulting mixture was boiled for 10 min and stirred for 3 h. Obtained precipitate was filtered off, crystallized from ethanol and dried in a vacuum over P_2O_5. Yield 0.19 g (95%). IR spectrum (vaseline oil), ν, cm^{-1}: 1590, 1492 (C=N, phenyl); 1542, 1465, 1437, 938 (C=O); 1394, 1348, 1024 (CH_3); 1172, 784, 765 [$(CH_2)_n$]; 1254 (C=C); 1218, 1103, 429, 416 (C_6H_4); 728 [$(CH_2)_n$–O]. IR spectrum (KBr), ν, cm^{-1}: 1592 (C=C); 1538, 1430, 940 (C=O); 1376, 1022 (CH_3); 1472, 1222, 1106, 720 (C_6H_4); 1578, 1172, 772 [$(CH_2)_n$]; 722 [$(CH_2)_n$–O]. ^1H NMR spectrum (CD_2Cl_2), δ, ppm (*J*, Hz): 0.91 t (6H, Me, *J* 6.8); 1.32 m (40H, CH_2); 1.81 m (4H, OCH_2CH_2); 4.02 t (4H, OCH_2, *J* 6.6); 6.93, 8.03 both d (4H, Ph, *J* 8.8); 7.25 s [1H, C(O)CH].

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