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SPECTRAL LUMINESCENCE PROPERTIES OF 1- AND 2-ALKYL(CYCLOALKYL) DERIVATIVES OF BENZO[f]QUINOLINE

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The absorption and fluorescence spectra of alcohol solutions of 3-aryl-substituted benzo[f]-quinolines were investigated, and the fluorescence quantum yields were measured. It was established that the indicated compounds have intense absorption in the UV region and fluorescence at 350-450 nm. The fluorescence quantum yields range from 5 to 70%, depending on the substituents. The introduction of aromatic substituents in the 1 and 3 positions of benzo-[f]quinoline ring raises the fluorescence quantum yields. A methyl group in the 2 position of the molecule leads to a decrease in the fluorescence quantum yield. Benzo[f]quinoline derivatives that contain a cyclopentene ring in the 1 and 2 positions fluoresce intensely ($\gamma = 40$-60%), while cyclohexene and cycloheptene condensed in the same positions cause a decrease in the fluorescence yield to 7-13%; this is associated with the three-dimensional structure of these molecules.

It is known that most of the organic luminophores that are in use have heterocyclic systems. The use of aryl-substituted pyrazolines, oxazoles, imidazoles, and other compounds as optical bleaches, fluorescent pigments, and the active substances of lasers [1] has served as an impetus for numerous new studies of the optical properties of complex organic molecules.

Little study has been devoted to the spectral luminescence characteristics of benzo[f]quinoline and its derivatives. The literature contains information regarding the existence of fluorescence in solutions of benzo-
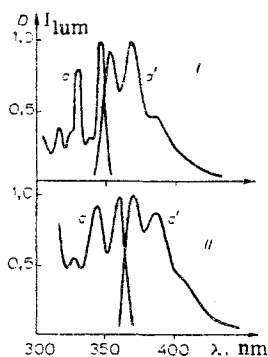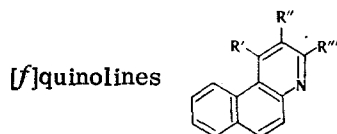

Fig. 1. Absorption (a) and fluorescence (a') spectra of alcohol solutions of benzo[f]quinoline (I) and 3-phenylbenzo[f]quinoline (II).

[f]quinolines

Com-pound	R'	R''	R'''	Absorption spectrum, λ_{max}, nm (log ε)	Fluorescence spectrum, λ_{max}, nm	Quantum yield, %
I	H	H	H	267, 317, 330, 346 (4,29; 3,45; 3,53; 3,58)	352, 369, 388	17
II	H	H	C_6H_5	280, 328, 343, 359 (4,78; 3,77; 3,99; 4,02)	369, 386, 407	50
III	H	H	p-$CH_3OC_6H_4$	285, 346, 364 (4,60; 4,12; 4,14)	376, 393, 418	71
IV	C_6H_5	H	C_6H_5	282, 347, 363 (4,69; 3,70; 3,72)	393	34
V	C_6H_5	H	p-$CH_3OC_6H_4$	287, 354, 367 (4,62; 3,93; 3,96)	402	45
VI	CH_3	H	C_6H_5	278, 328, 343, 360 (4,68; 3,47; 3,70; 3,74)	370, 386, 408	46
VII	CH_3	H	p-$CH_3OC_6H_4$	284, 346, 362 (4,60; 3,94; 3,95)	374, 392	66
VIII	C_2H_5	H	p-$CH_3OC_6H_4$	285, 347, 364 (4,57; 3,88; 3,89)	377, 393	66
IX	CH_3	CH_3	C_6H_5	258, 326, 338, 355 (4,63; 3,41; 3,66; 3,71)	372, 384	12
X	CH_3	CH_3	p-$CH_3OC_6H_4$	258, 328, 341, 356 (4,54; 3,50; 3,70; 3,74)	374, 388	7
XI	CH_3	H	p-$CH_3OCOC_6H_4$	280, 329, 345, 361 (4,69; 3,53; 3,76; 3,78)	371, 388, 412	48
XII	CH_3	H	p-HOC_6H_4	285, 346, 364 (4,61; 3,97; 3,97)	384, 395	50
XIII	CH_3	H	p-ClC_6H_4	280, 330, 344, 362 (4,73; 3,63; 3,82; 3,82)	373, 389, 413	30
XIV	CH_3	H	p-$NH_2C_6H_4$	294, 326, 364 (4,53; 4,15; 4,21)	475	29
XV	CH_3	H	p-$NO_2C_6H_4$	286, 318 (4,41; 4,12)	Does not fluoresce	
XVI	1,2-Cyclo-pentene		C_6H_5	260, 342, 360 (4,46; 3,46; 3,52)	370, 386	49
XVII	The same		p-$CH_3OC_6H_4$	265, 344, 360 (4,54; 3,83; 3,89)	370, 387	60
XVIII	1,2-Cyclo-hexene		C_6H_5	258, 322, 338, 354 (4,19; 3,00; 3,14; 3,20)	370, 384	7
XIX	The same		p-$CH_3OC_6H_4$	263, 340, 358 (4,64; 3,70; 3,73)	374, 385	5
XX	1,2-Cyclo-heptene		C_6H_5	260, 320, 342, 357 (4,58; 3,50; 3,78; 3,85)	373, 385	13
XXI	The same		p-$CH_3OC_6H_4$	263, 326, 344, 358 (4,64; 3,60; 3,78; 3,82)	377, 391	10

[f]quinoline and its 3-phenyl and 3-(p-tolyl) derivatives [2]. The effect of the solvent and the concentration of the hydrogen ions on the absorption and fluorescence spectra of benzo[f]quinoline was studied in [3]; it was observed that a bathochromic shift of the spectra accompanied by an increase in the fluorescence intensity occurs in acidic media and polar solvents. The spectral luminescence properties of some amino derivatives of 1,3-diarylbenzo[f]quinoline were analyzed in detail in [4].

Up until now there has been no systematic study of the dependence of the optical properties on the molecular structure in the benzo[f]quinoline series. The present research was devoted to an investigation of the spectral luminescence characteristics of 3-aryl derivatives of benzo[f]quinoline that contain alkyl and cycloalkyl substituents in the 1 and 2 positions.

The absorption spectra of the simplest representative of this series — benzo[f]quinoline — and its 3-aryl derivatives are similar to the spectrum of the isoelectronic phenanthrene [5]. They are represented by a system of three electronic bands: β (212-233 nm), p (258-290 nm), and α (328-370 nm). The latter band has a distinctly expressed vibrational structure (Table 1). In the present paper we will discuss only the α absorption bands and the fluorescence spectra of the investigated compounds. The absorption (long-wave bands) and fluorescence spectra of unsubstituted benzo[f]quinoline (I) and its 3-phenyl derivative (II) are presented in Fig. 1. It is apparent from Fig. 1 and Table 1 that the absorption and fluorescence spectra of benzoquinoline I have a sharply expressed vibrational structure and lie in the UV region. The introduction of substituents in the benzo[f]quinoline molecule leads to a long-wave shift of the spectra and a certain degree of smoothing out

of the structure. The bathochromic shift provides evidence that the long-wave absorption band and the fluorescence band of benzo[f]quinolines are due to transitions of the $\pi-\pi^*$ type [5]. The considerable magnitude of the extinction coefficient of the long-wave band indicates that the transition is allowed.

A vibrational structure also shows up distinctly in the fluorescence spectra of most of the compounds. The vibrational structure for the absorption spectra is determined primarily by the progression of the band at 1400 cm^{-1}, whereas the structure of the fluorescence spectra is determined primarily by the progression of the band at 1300 cm^{-1}. The indicated frequencies pertain to the fully symmetrical vibration of the skeleton of the molecule [5]. This fact serves as another confirmation of the $\pi-\pi^*$ electron nature of the examined absorption and fluorescence bands of benzo[f]quinoline derivatives. Lengthening of the conjugation chain by the introduction of two phenyl groups in the 1 and 3 positions leads to the disappearance of the vibrational structure of the fluorescence spectra. A similar effect with a simultaneous considerable bathochromic shift is observed for benzoquinoline XIV, which contains an amino group.

The existence of the intense luminescence of benzo[f]quinoline derivatives in ethanol can be explained, as in the case of quinoline [6], by the formation of a hydrogen bond between the nitrogen atom and the solvent. The hydrogen bond decreases the effect of the nonbonded electrons of nitrogen on the π-electron cloud of the molecule and thereby reduces the spin−orbital interaction and consequently the probability of interconversion.

The fluorescence quantum yields of the investigated compounds range from 5 to 70% (Table 1). Lengthening of the conjugation chain by the introduction of a phenyl group in the 3 position of benzo[f]quinoline leads to a considerable increase in the fluorescence yield (from 17 to 50%, I and II). The introduction of a bulky phenyl group in the 1 position of 3-phenylbenzo[f]quinoline leads to a decrease in the quantum yield (IV, V); this is evidently associated with steric hindrance. Alkyl groups in this position have practically no effect on the fluorescence yield (VI-VIII). The presence of another methyl group in the 2 position creates steric hindrance, which causes disruption of the coplanarity of the molecule; this should lead to an increase in the probability of intercombination transitions and consequently to quenching of the fluorescence (IX-X).

Alicyclic hydrocarbons condensed in the 1 and 2 positions give rise to a bathochromic shift of the long-wave absorption bands with a simultaneous increase in their intensities. The fluorescence quantum yield in this case increases considerably for XVI and XVII, which contain a cyclopentene ring. The introduction of six- and seven-membered rings leads to weakening of the fluorescence (XVIII-XXI). This is evidently associated with the fact that the four carbon atoms in the five-membered ring connected to the benzoquinoline ring are found in a single plane, and this promotes the greatest manifestation of the hyperconjugation effect. The hyperconjugation effect is displayed considerably more weakly in the less strained six- and seven-membered rings. In this case the steric effect, which increases as the size of the ring increases, is first and foremost. The certain increase in the fluorescence quantum yield of XX and XXI as compared with XVIII and XIX is evidently explained by an increase in the internal energy of cycloheptane as compared with cyclohexane [7, 8].

One should note the effect of substituents in the para position of the 3-phenyl ring on the fluorescence. Thus CH_3OCO and OH have practically no effect on the quantum yield, whereas Cl and NH_2 decrease it somewhat. The presence of a nitro group leads to complete quenching of the fluorescence; this is due to the high probability of intercombination conversion. The OCH_3 group (III, VII, and XVII) causes a considerable increase in the quantum yield.

EXPERIMENTAL

The absorption spectra of solutions of the compounds were recorded with Unicam SP-800 and Specord UV-Vis spectrophotometers. The excitation and fluorescence spectra and the quantum yields were measured with a Fika-55 absolute spectrofluorimeter. The luminescence was excited at 350 nm (II-XXI). The luminescence of benzo[f]quinoline I was excited at 346 nm. The solvent was absolute ethanol. A solution of 3-amino-N-methylphthalimide [9] was used as the standard in the measurement of the fluorescence quantum yields.

The 1- and 2-alkyl(cycloalkyl)-3-phenylbenzo[f]quinolines were obtained by reaction of arylidene-2-naphthylamines with aliphatic, aliphatic-aromatic, and cyclic ketones [10-12] and were purified by repeated crystallization from alcohol and toluene. The individuality of the products was monitored by thin-layer chromatography in a loose layer of Al_2O_3 (elution with benzene and development with iodine vapors) and also by means of the excitation spectra.

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# RESEARCH OF NAPHTHYRIDINES

IX.† ACID−BASE TRANSFORMATIONS OF BENZO[b]-1,8-NAPHTHYRID-10-ONES

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It is shown by means of the UV spectra that a singly charged ion due to protonation at the $N_{(4)}$ atom develops when benzo[b]-1,8-naphthyrid-10-ones are dissolved in dilute mineral acids. The oxygen of the carbonyl group is also protonated in 96% sulfuric acid. Salts of the phenoxide type are formed in the reaction of these compounds with aqueous sodium hydroxide solutions. The pK_a values of benzo[b]-1,8-naphthyrid-10-ones determined spectrophotometrically in a sulfuric acid−water system range from −4.69 to −5.69, depending on the substituent in the 8 position, and correlate with the Hammett σ_p constants.

It is known that 9-acridone displays weak basic properties and gives a cation of the acridinium type when it is dissolved in sulfuric acid. In this case the proton adds to the oxygen atom of the carbonyl group [2]. In order to study the previously uninvestigated acid−base transformations of benzo[b]-1,8-naphthyrid-10-ones and to compare their properties with those of 9-acridone we accomplished the synthesis of several compounds of this series (Ia-e) by cyclization of 2-anilinonicotinic acids in polyphosphoric acid (PPA) or sulfuric acid.
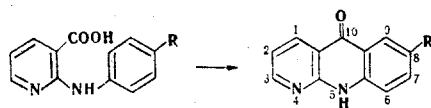
I a R=H; b R=CH₃; c R=CH₃O; d R=Cl; e R=Br

Like 9-acridone [2, 3], benzonaphthyridones Ia-e exist in the oxo rather than hydroxy form, as evidenced by the data from the IR spectra of solutions in CCl_4, which contain a ν_{NH} band at 3440 cm⁻¹ and a ν_{CO} band at 1640 cm⁻¹ but no hydroxyl group band.‡ Maxima are observed in the UV spectra of benzonaphthyridones Ia-e (see the spectra of Ia in Figs. 1 and 2) at 235, 256, 385, and 400 nm, and they are very similar to the spectrum

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†See [1] for communication VIII.

‡ The bands were assigned in accordance with [3].