

anhydride was removed by distillation, 20 ml of water was added, and the mixture was saturated with sodium carbonate. The reaction products were extracted with ether, the extracts were dried with magnesium sulfate, and the solvent was removed by distillation. Crystallization of the residue from hexane gave 0.2 g (50%) of amide XI as pale rose granular crystals with mp 114.5–130° and R_f 0.75. IR spectrum, cm^{-1} : 3015 w (C-H_{arom}), 2978 w, 2938 w and 2885 w (ν of CH bonds of the CH_3 group), 1722 m (C=O), 1602 m and 1542 s (C=C_{arom}), 1465 m ($\delta_{\text{AS}} \text{CH}_3$), 1365 m ($\delta_{\text{S}} \text{CH}_3$), and 682 s (monosubstituted benzene ring). Found: N 8.7%. $\text{C}_{21}\text{H}_{18}\text{N}_2\text{O}$. Calculated: N 8.9%.

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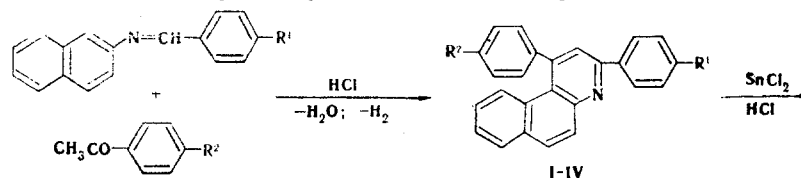
SYNTHESIS AND SPECTRAL-LUMINESCENCE PROPERTIES OF SOME SUBSTITUTED 1,3-DIARYLBENZO[f]QUINOLINES

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Amino derivatives of 1,3-diarylbenzo[f]quinoline were synthesized and subjected to reaction with methyl vinyl ketone in the presence of catalytic amounts of concentrated HCl to give the corresponding (3'-oxobutyl)amino-phenyl derivatives. The electronic absorption and fluorescence spectra were studied, and the absolute fluorescence quantum yields of the synthesized compounds were determined. A relationship between the position and intensity of the absorption bands and the electron-donor substituents was uncovered, and a substantial effect of the nature of the solvent on the fluorescent spectra was established.

The available data on the luminescence properties of benzo[f]quinoline and its derivatives are limited [1, 2]. In the present paper we describe the synthesis and electronic absorption and emission spectra of some amines and amino ketones of 1,3-diarylbenzo[f]quinoline (V-XII) (Table 1). Amines V-VIII were obtained by reduction of the corresponding nitro derivatives (I-IV), which were synthesized by catalytic condensation of arylidene- β -naphthylamines with aliphatic-aromatic ketones [3, 4]. Amino ketones IX-XII were obtained by reaction of amines V-VIII with methyl vinyl ketone in the presence of a catalyst.



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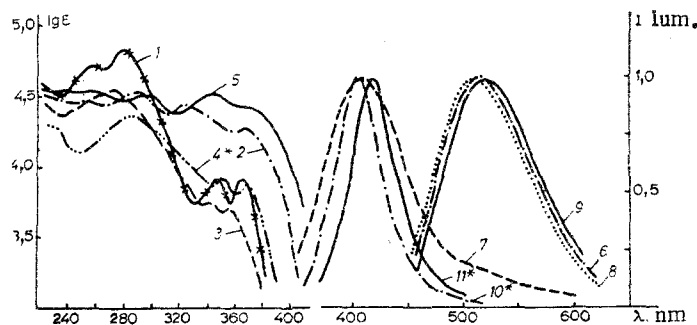
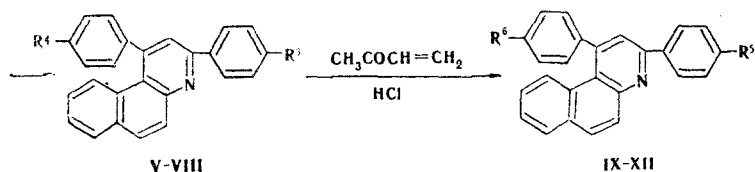


Fig. 1. Absorption spectra (1-5) and fluorescence spectra (6-11) of 1,3-diarylbenzo[f]quinolines in ethanol: 1) 1,3-diphenylbenzo[f]quinoline; 2) 4*), 6), and 10*) 1-phenyl-3-(p-aminophenyl)benzo[f]quinoline (V); 3) and 7) 1-(p-aminophenyl)-3-phenylbenzo[f]quinoline (VI); 5), 9), and 11*) 1-phenyl-3-[p-(3'-oxobutyl)aminophenyl]benzo[f]quinoline (IX); 8) 1-(p-aminophenyl)-3-(p-dimethylaminophenyl)benzo[f]quinoline (VIII).



I $R^1=NO_2$, $R^2=H$; II $R^1=H$, $R^2=NO_2$; III $R^1=R^2=NO_2$; IV $R^1=N(CH_3)_2$, $R^2=NO_2$;
V $R^3=NH_2$, $R^4=H$; VI $R^3=H$, $R^4=NH_2$; VII $R^3=R^4=NH_2$; VIII $R^3=N(CH_3)_2$, $R^4=NH_2$;
IX $R^5=X$, $R^6=H$; X $R^5=H$, $R^6=X$; XI $R^5=R^6=X$; XII $R^5=N(CH_3)_2$, $R^6=X$, where $X=NHCH_2CH_2COCH_3$.

A number of bands of moderate intensity appear in the absorption spectra of the investigated compounds. The first two long-wave bands, the interval between which is $1200-1300\text{ cm}^{-1}$ (these bands are practically unresolved in ethanol but are sufficiently distinctly expressed in nonpolar solvents), can be interpreted as the α band [5] (the $'L_b$ band in the Platt classification) and its vibrational satellite. The intense band at $280-298\text{ nm}$ in the spectra of the amines and at $282-299\text{ nm}$ in the spectra of the amino ketones is apparently the p band ($'L_A$ band).

The three markedly overlapped bands at $200-260\text{ nm}$ correspond to the three electron transitions ($'B_b$, S_4 , and S_5 [6]) of phenanthrene. The $'B_b$ transition for phenanthrene, according to [6, 7], is localized at 251 nm . The band at $253-257\text{ nm}$ in the spectra of benzo[f]quinolines is evidently the β band ($'B_b$ band). The shorter-wave bands (~ 230 and $\sim 210\text{ nm}$) can be interpreted as S_4 and S_5 bands.

The position and relative intensity of the bands depend substantially on the position of the electron-donor substituent. Thus, in the case of 1-(p-aminophenyl)-3-phenylbenzo[f]quinoline (VI) the absorption spectrum practically coincides with respect to position and intensity with the absorption spectrum of 1,3-diphenylbenzo[f]quinoline (Fig. 1). The introduction of an electron-donor substituent in the 3 position of the benzo[f]quinoline ring (V) causes a bathochromic shift of the long-wave absorption band of 9 nm and increases its intensity by a factor greater than two. The p band also experiences a bathochromic shift (of 13 nm), whereas the position of the β band remains practically unchanged. Another band at $329-333\text{ nm}$ appears in the spectra of 3- and 1,3-substituted benzo[f]quinolines (V and VII), and another band appears at 345 nm in the spectrum of 1-(p-aminophenyl)-3-(p-dimethylaminophenyl)benzo[f]quinoline (VIII).

In the case of (3'-oxobutyl)aminophenyl derivatives of benzo[f]quinoline the introduction of a keto group does not have an appreciable effect on the spectrum of the starting amine; a slight ($2-4\text{ nm}$) bathochromic shift of the α , p, and β bands is observed. The band at 333 nm , which is sensitive to substitution in the phenyl group, is shifted to $341-345\text{ nm}$. One

TABLE 1. Characteristics of 1,3-Diarylbenzo[flquinolines

Com- pound	mp, °C	Empirical formula	Found, %			Calc., %			UV spectra, λ_{\max} , nm (log ϵ)		λ_{\max} , nm (ethanol)	B, %	IR spectra, cm ⁻¹				Yield, %
			C	H	N	C	H	N					ν_{N-H}	δ_{N-H}	ν_{C-N}	$\nu_{C=O}$	
V	192	C ₂₅ H ₁₈ N ₂	86.5	5.2	8.1	86.7	5.1	8.1	295 (4.53)	333 (4.42)	373 (4.26)	45.0	3470 3330 3190	1615	1300		50
VI	189	C ₂₅ H ₁₈ N ₂	86.5	5.3	8.0	86.7	5.1	8.1	280 (4.54)	—	360 (3.76)	27.5	3450 3340 3220	1620	1285		47
VII	231—232	C ₂₅ H ₁₉ N ₂	83.0	4.2	11.5	83.1	4.2	11.6	297 (4.60)	329 (4.56)	367 (4.33)	37.5	3475 3380 3220	1615	1290		49
VIII	255—256	C ₂₇ H ₂₂ N ₃	83.2	6.0	10.8	83.3	5.9	10.8	298 (4.57)	345 (4.63)	371 (4.51)	62.5	3470 3340 3225	1630	1290		49
IX	144	C ₂₉ H ₂₄ N ₂ O	83.9	6.0	6.5	83.6	5.7	6.7	298 (4.53)	341 (4.51)	376 (4.44)	60.0	3410		1710		47
X	178	C ₂₉ H ₂₄ N ₂ O	83.6	5.9	6.6	83.6	5.7	6.7	282 (4.65)	343 (4.02)	363 (4.02)	7.5	3400		1705		50
XI	167—168	C ₃₃ H ₃₁ N ₃ O ₂	79.1	6.4	8.7	79.4	6.2	8.4	299 (4.32)	340 (4.32)	371 (4.22)	30.0	3400		1705		51
XII	187—188	C ₃₁ H ₂₉ N ₃ O	81.0	6.2	9.1	81.0	6.3	9.1	298 (4.86)	345 (4.89)	371 (4.77)	37.5	3400		1705		39

cannot exclude the possibility that this band is due to a $\pi-\pi^*$ transition in a phenyl group excited by a substituent.

All of the synthesized compounds luminesce well in solution. The fluorescence spectrum is a single, quite broad, structureless band. The position of the fluorescence maximum and its half width depend substantially on the nature of the solvent (in petroleum ether the fluorescence maxima of V and IX are found at 400-420 nm, whereas in ethanol they are situated at 500-520 nm); however, in the absorption spectra the shift of the long-wave band at 370 nm does not exceed several nanometers. This pronounced effect of solvents on the **fluorescence** spectra is associated with intensification of the intermolecular interactions in the excited state. This may be due either to the formation of a complex with the solvent through a hydrogen bond (an exciplex) or to orientation interaction effects associated with a change in the dipole moment in the excited state and reorientation of the solvent molecules during the lifetime of the excited state [8]. We feel that the first assumption is more likely, inasmuch as the fluorescence spectrum of 1-(p-aminophenyl)-3-phenylbenzo[f]quinoline (VI) in ethanol consists of two bands - a stronger band at 408 nm and a weaker band at 520 nm. These bands apparently correspond to the unexcited molecule (at 408 nm) and the exciplex (at 520 nm).

The absolute fluorescence quantum yields (B) of the investigated compounds range from 30 to 60% (Table 1). A lower quantum yield is characteristic for compounds that have lower intensities of the long-wave absorption bands.

The fluorescence yield $B = \frac{f}{f+d}$ where f is the probability of the $S_1 \rightarrow S_0$ emissive transition, and d is the overall probability of emissionless transitions from the S_1 level. It is well known [9] that the probability of an emissive transition is proportional to the oscillator force for a given transition, which can be determined from the Krawetz integral $\phi = 4.32 \cdot 10^{-9} \int \epsilon dv$. The observed differences in the fluorescence quantum yields can be explained by the lower probability of emissive transitions in the compounds. The probability (d) of emissionless transitions apparently depends only slightly on the molecular structure.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The UV spectra of ethanol solutions were recorded with a Specord UV-vis spectrophotometer. The fluorescence spectra were measured with a Fika-55 spectrofluorimeter. The absolute fluorescence quantum yield was determined by a relative method. A solution of rhodamine 6Zh in ethanol, the fluorescence quantum yield of which is 83% [10], was used as the standard.

Data characterizing V-XII are presented in Table 1.

1-Phenyl-3-(p-nitrophenyl)-(I), 1-p-Nitrophenyl-3-phenyl-(II), and 1,3-Di(p-nitrophenyl)benzo[f]quinoline (III). These compounds were obtained by the methods in [3, 4].

1-(p-Nitrophenyl)-3-(p-dimethylaminophenyl)benzo[f]quinoline (IV). A mixture of 11 g (0.04 mole) of p-dimethylaminobenzal- β -naphthylamine, 6.6 g (0.04 mole) of p-nitroacetophenone, 20 ml of ethanol, 10 ml of nitrobenzene, and 10 ml of concentrated HCl was heated at 100° for 25 h, after which it was cooled and treated with an aqueous alcohol solution of ammonia and washed successively with acetone and aqueous alcohol. The red crystalline product was isolated to give 6.2 g (37%) of a substance with mp 248-249° (from benzene). Found: C 77.4; H 5.1; N 10.0%. $C_{27}H_{21}N_3O_2$. Calculated: C 77.3; H 5.0; N 10.0%. IR spectrum: ν_{NO_2} 1540 and 1345 cm^{-1} .

1-(p-Aminophenyl)-3-(p-dimethylaminophenyl)benzo[f]quinoline (VIII). A solution of 90 g (0.4 mole) of stannous chloride dihydrate in 100 ml of concentrated HCl was added slowly at 100° to a suspension of 21 g (0.05 mole) of IV in 600 ml of p-C₃H₇OH, after which the mixture was maintained under these conditions for 2 h. It was then cooled and treated at 5-10° with 40% NaOH until the color of the reaction mass changed from red to bright yellow (pH 13). The butanol layer was separated from the precipitate, washed with water until it gave a neutral reaction, and dried with Na₂SO₄. The solvent was removed by distillation to give VIII. An additional amount of VIII was extracted from the precipitate with toluene in a Soxhlet apparatus. The overall yield was 9.6 g (49%).

Amines V-VII. These compounds were obtained by the methods in [3, 11].

1-[p-(3'-Oxobutyl)aminophenyl]-3-(p-dimethylaminophenyl)benzo[f]quinoline (XII). An alcohol-toluene solution (1:2) of 1.95 g (5 mmole) of amine VIII, 7.5 mmole of methyl vinyl ketone, and five drops of concentrated HCl was heated on a boiling-water bath for 4 h, after which it was cooled and the resulting precipitate was removed by filtration, neutralized with an aqueous-alcohol solution of ammonia, and recrystallized from alcohol or toluene to give 0.9 g (39%) of product.

Amino Ketones IX-XI. These compounds were similarly obtained; the reaction time was 10-15 min.

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RESEARCH ON IMIDAZO[1,2-a]BENZIMIDAZOLE DERIVATIVES

XII.* 3-ACYL-SUBSTITUTED IMIDAZO[1,2-a]BENZIMIDAZOLES

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UDC 547.785.5

Stable 3-acetyl derivatives of imidazo[1,2-a]benzimidazole were synthesized by the action of acetic anhydride on 2,9-disubstituted imidazo[1,2-a]benzimidazole. The former were also obtained by cyclization of 1-alkyl(aralkyl)-3-acylmethyl-2-iminobenzimidazoline hydrobromides in acetic anhydride in the presence of anhydrous sodium acetate. 3-Benzoyl-substituted imidazo[1,2-a]benzimidazoles, which are unstable in acidic media, were synthesized by the action of benzoyl chloride in the presence of pyridine or excess starting imidazo[1,2-a]benzimidazole.

Imidazo[1,2-a]benzimidazoles (Ia-e), like many similarly constructed systems with a nitrogen atom in common [2-4], are readily acetylated in the 3 position on brief heating with acetic anhydride.

*See [1] for communication XI.

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