(−)-Menthone, with bp 94°C (17 mm), n_D^{20} 1.4502, and $[\alpha]_D^{20}$ −28°, was obtained in 76% yield by oxidation of l-menthol with a chromic acid mixture [9].

2-Isobutylcyclohexanone was obtained by refluxing 0.1 mole of 1-pyrrolidinyl-1-cyclohexene and isobutyl iodide in absolute CH_3OH for 5 h. The methanol was removed by distillation, 80 ml of 2 N HCl was added to the dry residue, and the mixture was refluxed for 1.5 h. It was then cooled and extracted with ether, and the ether extract was washed with water and dried over Na_2SO_4. The solvent was removed, and the residue was vacuum distilled to give 4.6 g (30%) of a product with bp 87-88°C (13 mm) and n_D^{20} 1.4525 (bp 77-78°C, 5 mm [11]).

The enamino ketones (Table 1) were obtained by the methods in [2-4].

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SPECTRAL-LUMINESCENCE AND GENERATION CHARACTERISTICS OF 1-R-VINYL-3-ARYL(HETERYL)BENZO[f]QUINOLINES

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UDC 535.372:547.832.5

The absorption and fluorescence spectra and the fluorescence quantum yields of 1-R-vinyl derivatives of benzo[f]quinoline containing aryl and 2-, 4-, and 6-quinolyl groups in the vinylene grouping and in the 3 position were studied. The relationship between the spectral-luminescence characteristics and the structures of the molecules was examined. It was established that solutions of compounds that contain a dimethylamino group attached to the phenyl ring give forced emission when they are excited with the second harmonic of a ruby laser. The effect of the solvent on the spectral-luminescence and generation characteristics of the indicated compounds was investigated.

Continuing our research on the effect of the structural factors on the spectral-luminescence properties of benzo[f]quinoline derivatives [1, 2], we investigated 1-R-vinyl-3-aryl(heteryl)benzo[f]quinolines. The latter were obtained by reaction of arylidene-2-naphthylamine with α,β-unsaturated ketones [3, 4] and by condensation of 1-methyl derivatives of benzo[f]quinoline with aldehydes or anils of the aromatic and heterocyclic series [5, 6].

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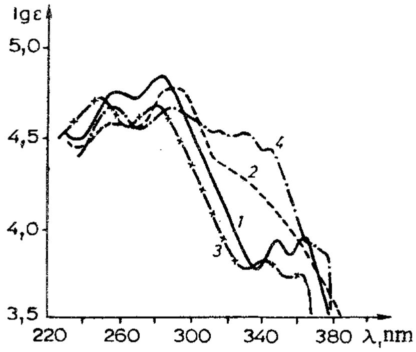


Fig. 1. UV spectra of benzo[f]quinoline derivatives (in alcohol): 1) 1,3-diphenylbenzo[f]quinoline (I); 2) 1-styryl-3-phenylbenzo[f]quinoline (II); 3) 1-(α-methylstyryl)-3-phenylbenzo[f]quinoline (XII); 4) 1-styryl-3-(2-quinolyl)benzo[f]quinoline (XX).

The absorption spectra of solutions of the compounds were recorded with a UV-vis spectrophotometer, and the fluorescence spectra were recorded with a Fica-55 absolute spectrofluorimeter. The absolute fluorescence quantum yields were measured by a relative method. A solution of 3-amino-N-methylphthalimide in ethanol served as the standard. Ethanol, dimethyl sulfoxide (DMSO), and cyclohexane, purified by standard methods, were used as the solvents.

It is known that the absorption spectrum of 1,3-diphenylbenzo[f]quinoline (I) (Fig. 1, spectrum 1) consists of three bands [2]. The long-wave band, which has a vibrational structure [347 and 364 nm (log ε 3.92 and 3.94)], was interpreted as an α band ('L_b in the Platt designation). The shorter-wave bands at 282 and 259 nm (log ε 4.88 and 4.76) are p and β bands ('L_a and 'B_b), respectively.

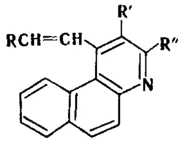
The transition to the vinyl derivatives is accompanied by an appreciable change in the absorption spectra (Table 1). The introduction of a chromophore that includes a dimethylamino grouping increases the conjugation chain, and this leads to a change in the spectral position of the p and β bands and to the appearance of intense absorption in the region of the α band (Fig. 1, curve 2).

The introduction of substituents in the phenyl rings of 1-styryl-3-phenylbenzo[f]quinoline (II) affects the electronic absorption spectrum. Substituents with negative inductive and positive conjugation effects (OCH_3 and halogens) give rise to a slight bathochromic shift of the α and p absorption bands virtually without changing the spectral pattern (III-VI, Table 1). Under the influence of the electron-donor p-dimethylamino group the spectrum becomes more complicated (VII and VIII). When this substituent is introduced in the styryl grouping, an increase in the absorption intensity and an apprecialbe bathochromic shift of the long-wave absorption band (VII) are observed. This complication of the spectrum is apparently due to the possibility of absorption with charge transfer and the participation of the electrons of the dimethylamino group. In the case of electron-acceptor substituents (R = p-nitrophenyl and 2- and 4-quinolyl, IX-XI), one observes drawing together of the β and p bands and the formation of a rather broad absorption band at 270 nm.

A methyl group in the α position of the vinylene grouping (XII) or in the 2 position of the benzoquinoline ring (XIII-XV) decreases the intensity of the absorption in the region of the long-wave band and has a slight effect on the position and intensity of the β and p bands; the spectrum becomes similar to the spectrum of benzoquinoline I (Fig. 1, curve 3). This is evidently associated with the fact that the methyl group increases the steric hindrance that exists in the styryl molecule, thereby removing the styryl grouping from conjugation [7]. A similar effect is observed when hydroxyl groups are introduced in the ortho position of the phenyl rings (XVI-XIX). In this case the benzo[f]quinoline ring acts as an independent chromophore.

The spectra of 1-(R-vinyl)-3-(2-quinolyl)benzo[f]quinolines (XX-XXIV) contain, in addition to absorption bands of the benzo[f]quinoline ring, three rather intense maxima at 315-

TABLE 1. Spectral-Luminescence Characteristics of 1-R-Vinyl-3-aryl(heteryl)benzo[f]quinolines



Compound	R	R'	R''	Absorption (ethanol), λ_{max}, nm (log ε)	Fluorescence (DMSO)	
					λ_{max}, nm	Quantum yield, %
1	2	3	4	5	6	7
II	C_6H_5	H	C_6H_5	259, 290, 340 (4,57; 4,80; 4,20)	425	13,2
III	C_6H_5	H	p-$CH_3OC_6H_4$	255, 299, 360 (4,46; 4,66; 4,00)	460	12,4
IV	p-$CH_3OC_6H_4$	H	p-BrC_6H_4	260, 295, 350 (4,56; 4,69; 4,40)	470	~1
V	p-BrC_6H_4	H	p-$CH_3OC_6H_4$	260, 297, 370 (4,52; 4,64; 3,97)	460	8,8
VI	p-FC_6H_4	H	C_6H_4—C_6H_5	263, 300, 366 (4,41; 4,82; 4,11)	440	14,3
VII	p-$(CH_3)_2NC_6H_4$	H	C_6H_5	257, 288, 377 (4,57; 4,60; 4,24)	595	18,2
VIII	p-BrC_6H_4	H	p-$(CH_3)_2NC_6H_4$	285—290, 368 (4,17; 4,75)	605	24,2
IX	p-$NO_2C_6H_4$	H	C_6H_5	277, 344 (4,02; 3,73)	No fluorescence	
X	2-Quinolyl	H	C_6H_5	260—270, 338 (4,73; 4,40)	—	—
XI	4-Quinolyl	H	C_6H_5	272, 340 (3,96; 3,46)	458	12,1
XII*				250, 282, 345, 362 (4,70; 4,68; 3,83; 3,72)	410	8,0
XIII	C_6H_5	CH_3	C_6H_5	263, 294, 325, 341, 357 (4,59; 4,37; 3,92; 3,89; 3,85)	372, 391, 412 shoulder	3,5
XIV	C_6H_5	CH_3	p-$CH_3OC_6H_4$	268, 294, 342, 360 (4,64; 4,53; 3,95; 3,94)	376, 393, 420	6,7
XV	C_6H_5	CH_3	p-ClC_6H_4	267, 294, 324, 342, 359 (4,64; 4,48; 4,01; 3,97; 3,88)	377, 397, 422	3,1
XVI	o-OHC_6H_4	H	C_6H_5	255, 284, 345 (4,54; 4,63; 4,11)	468, 685	3,0
XVII	o-OHC_6H_4	H	o-OHC_6H_4	258, 284, 325, 355, 373 (4,59; 4,63; 4,23; 4,09; 4,17)	415	~1
XVIII	o-OHC_6H_4	H	p-$CH_3OC_6H_4$	262, 289, 350, 370 (4,53; 4,64; 4,23; 4,13)	465, 670	3,5
XIX	o-OHC_6H_4	H	p-BrC_6H_4	262, 290, 350 (4,64; 4,76; 4,32)	480, 670	2,3
XX	C_6H_5	H	2-Quinolyl	257, 287, 316, 329, 344, 374 (4,68; 4,69; 4,53; 4,53; 4,45; 3,88)	425	11,7
XXI	6-Quinolyl	H	2-Quinolyl	259, 287, 319, 330, 344, 374 (4,77; 4,71; 4,58; 4,62; 4,61; 3,90)	430	10,0
XXII	p-$NO_2C_6H_4$	H	2-Quinolyl	250, 275, 317, 329, 342, 369 †	No fluorescence	
XXIII	2-Quinolyl	H	2-Quinolyl	265—285, 315, 330, 345, 378 (4,78; 4,59; 4,62; 4,60; 4,06)	442	11,7
XXIV	4-Quinolyl	H	2-Quinolyl	265—285, 320, 331, 344, 378 (4,69; 4,54; 4,57; 4,50; 3,96)	448	11,3

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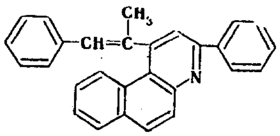


†The extinction for XXII was not calculated because of its low solubility.

320, 330, and 344 nm (Fig. 1, curve 4), which should evidently be assigned to the absorption of the quinolyl group [8]. The additivity of the absorption spectra of XX-XXIV attests to the absence of conjugation of the quinolyl substituent in the 3 position. The R group in the vinyl portion affects only the position and ratio of the intensities of the p and β bands. The spectra of XX and XXI (R = phenyl and 6-quinolyl) are similar to one another (Table 1).

As in the case of the analogous 3-phenyl derivatives (IX-XI), drawing together of the β and p bands and the formation of a broad absorption band at 270 nm are observed on passing to XXII-XXIV (R = p-nitrophenyl and 2- and 4-quinolyl); in the case of XXI a low-intensity maximum (~250 nm) appears on the slope of this band.

Most of the investigated vinyl derivatives of benzo[f]quinoline luminesce in solution (Table 1). The absolute fluorescence quantum yields of alcohol solutions do not exceed 10%. This decrease in the fluorescence quantum yields of the vinyl derivatives as compared with the aryl derivatives [1] can be explained by the absence of molecular rigidity, which gives rise to degradation of the electron excitation energy [9]. The use of more viscous DMSO as the solvent hinders rotation of the vinylene grouping, thereby raising the fluorescence quantum yield (Table 1). The fluorescence spectra of the vinyl derivatives of benzo[f]quinoline are rather broad structureless bands that are shifted bathochromically relative to the spectrum of 1,3-diphenylbenzo[f]quinoline (λ_{fl} 397 nm, fluorescence quantum yield 30% in DMSO). Substituents in the phenyl rings cause a bathochromic shift of the fluorescence band. The halogens, inasmuch as they are heavy atoms, substantially change the probability of the single—triplet conversion, thereby lowering the fluorescence quantum yield. It must be noted that halogens introduced into the styryl portion of the molecule (V and VI) have less of a quenching effect than halogens in the 3 position of the phenyl ring (IV, XV, and XIX). Substituents that decrease the conjugation in the styryl molecule (XII-XIX and XX-XXIV) lead to a decrease in the fluorescence quantum yields. This is displayed most vividly in the case of introduction of a methyl group in the 2 position of the benzo[f]quinoline ring and of o-hydroxyl groups in the styryl and phenyl rings; conjugation of the benzoquinoline ring with the substituents in both the 1 and 3 positions is disrupted, and this leads to the appearance of a benzoquinoline structure (XIII-XV) in both the fluorescence and absorption spectra. The lower fluorescence quantum yields of these compounds as compared with the quantum yield of unsubstituted benzo[f]quinoline (17%) [2] are due to the additional expenditure of energy for the intramolecular vibrations of the terminal substituents. Additional quenching of the fluorescence due to interaction of the hydroxyl groups in the ortho position of the phenyl rings with DMSO of the $-O-H\ldots O{=}S(CH_3)_2$ type is possible in the case of XVI-XIX. The appearance of additional weak fluorescence in the long-wave region of the spectra (XVI, XVIII, and XIX) is evidently due to the formation of an exiplex.

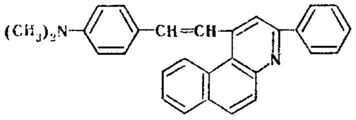
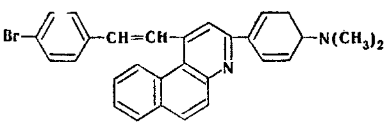
A methoxy group in the para position of the 3-phenyl ring somewhat increases the fluorescence quantum yield (XIV). The presence of a nitro group leads to complete quenching of the fluorescence (IX and XX).

The introduction of an electron-donor $(CH_3)_2N$ substituent in the phenyl ring in the 3 position (VIII) or in the vinyl portion of the molecule (VII) leads to a pronounced bathochromic shift and broadening of the fluorescence spectrum; the fluorescence quantum yield increases in this case.

The studies showed that the compounds generate when they are excited with the second harmonic of a ruby laser (λ_b = 347 nm) operating under single-pulse conditions. The generation band lies on the long-wave slope of the fluorescence spectrum (Table 2). The positions of the maxima of the fluorescence and generation spectra of VII and VIII depend substantially on the nature of the solvent. Thus for VII passing from DMSO to cyclohexane leads to a 145 nm shift (from 595 to 450 nm) of the fluorescence maximum, whereas the shift of the long-wave band in the absorption spectra does not exceed a few nanometers. This significant shift in the fluorescence spectra is due to reinforcement of the intermolecular interactions in the excited state. These are most likely relaxation effects of the orientation interaction that are associated with a change in the dipole moment of the fluorescing molecule during excitation [10].

The short-wave shift of the fluorescence spectrum as the polarity of the solvent decreases is accompanied by a corresponding shift of the generation spectrum (Table 2). Forced emission is absent only in the case of benzene solutions, the fluorescence quantum yields of which are very low (~1%).

TABLE 2. Spectral-Luminescence and Generation Characteristics of Styryl Derivatives of Benzo[f]quinoline with a Dimethylamino Group in the Phenyl Ring

No.	Compound	Solvent	γ, %	λ_{max}^{tor}, nm	λ_{max}^{fl}, nm	λ_{max}^{gen}, nm	$\Delta\lambda_{gen}$, nm
VII		DMSO	23	380	590	605	575—685
		Ethanol	5	370	570	590	560—640
		Acetone	6	372	560	582	560—620
		Benzene	~1	370	495	—	
VIII		DMSO	26	370	610	610	575—675
		Ethanol	7	370	578	595	
		Acetone	8	365	570	587	565—620
		Benzene	~1	365	505	—	

The great width of the fluorescence spectra of VII and VIII made it possible to obtain considerable limits of rearrangement of the generation spectrum when a diffraction grating was used in the resonator of a liquid laser. Thus the generation spectrum of VII in DMSO undergoes a rearrangement from 575 to 685 nm, as compared with a rearrangement from 575 to 675 nm for VIII in the same solvent. Thus when a single solution is used, one can obtain a continuous rearrangement of the generation spectrum of more than 100 nm.

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