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SYNTHESIS AND SPECTRAL CHARACTERISTICS OF 1-(3-PYRIDYL)-3-ARYL-8-NITRO(AMINO)BENZO-[f]QUINOLINES

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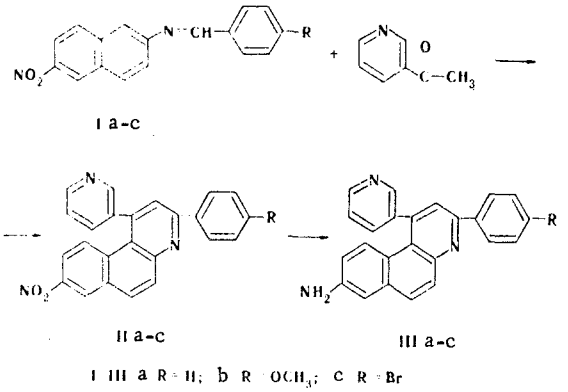
1-(3-pyridyl)-3-aryl-8-aminobenzo[f]quinolines were synthesized by reduction with tin in acidic media of 1-(3-pyridyl)-3-aryl-8-nitrobenzo[f]quinolines obtained by catalytic condensation of arylidene(6-nitro)-2-naphthylamines with acetylpyridine. The structures of the compounds were proved by a set of data from elementary analysis and IR, UV, and mass spectroscopy. The change in the luminescence of 1-(3-pyridyl)-3-aryl-8-aminobenzo[f]quinoline as a function of the solvent was studied.

Continuing our study of the spectral properties of benzo[f]quinoline derivatives [1] we synthesized 1-(3-pyridyl)-3-arylbenzo[f]quinolines containing amino and nitro groups in the 8 position:



I a-c

II a-c

III a-c

I, III a R = H; b R = OCH_3; c R = Br

The 1-(3-pyridyl)-3-aryl-8-nitrobenzo[f]quinolines (II) were obtained by catalytic condensation of arylidene-(6-nitro)-2-naphthylamine (I) with acetylpyridine. The 1-(3-pyridyl)-3-aryl-8-aminobenzo[f]quinolines (III) were synthesized by reduction of the corresponding nitro derivatives (II) with stannous chloride in glacial acetic acid (Table 1).

The structures of the compounds obtained were confirmed by the results of elementary analysis and the data from the IR, UV, and mass spectra. The IR spectra of II and III contain absorption bands characteristic for the stretch ing and deformation vibrations of NO_2 (1520-1530 and 1335-1340 cm^{-1}) and NH_2 (3400-3500 and 1630-1640 cm^{-1} groups, respectively.

Maximally intense molecular-ion peaks are observed in the mass spectra of II and III (Fig. 1). The agreement between the m/e values of the molecular-ion peaks and the molecular weights confirms the proposed

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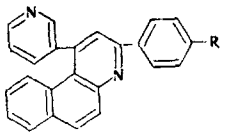
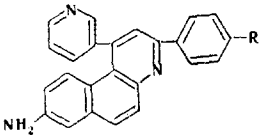
TABLE 1. Characteristics of the Synthesized Compounds

Compound	R	mp, °C	Found, %			Empirical formula	Calculated, %			Yield, %
			C	H	N		C	H	N	
IIa	H	243—244	76,6	4,2	11,2	$C_{24}H_{15}N_3O_2$	76,5	4,0	11,1	37
IIb	OCH_3	290—291	73,6	4,2	9,9	$C_{25}H_{17}N_3O_3$	73,7	4,2	10,3	45
IIc	Br	333—334	63,4	3,4	9,1	$C_{24}H_{14}N_3O_2Br$[a]	63,2	3,1	9,2	27
IIIa	H	247—248	82,8	5,1	11,7	$C_{24}H_{17}N_3$	82,9	4,9	12,1	78
IIIb	OCH_3	250—251	79,8	5,1	10,8	$C_{25}H_{19}N_3O$	79,6	5,0	11,1	71
IIIc	Br	282—283	67,8	4,3	10,1	$C_{24}H_{16}N_3Br$[b]	67,5	3,8	9,9	66

[a]Found: Br 17.5%. Calculated: Br 17.5%. [b]Found: Br 19.3%. Calculated: Br 18.8%.

TABLE 2. Spectral-Luminescence Characteristics

Formula	R	Absorption, λ_{max}, nm ($\varepsilon \cdot 10^{-4}$), ethanol	Luminescence					
			ethanol		DMSO		benzene	
			λ_{max}, nm	η, %	λ_{max}, nm	η, %	λ_{max}, nm	η, %
 A a-c	H	213 (3,34); 261 (4,08); 282 (4,54); 350 (0,65); 366 (0,74)	396	32	396	31	392	34
	OCH_3	218 (4,10); 277 (5,01); 289 (5,39); 354 (1,44); 369 (1,52)	408	43	410	44	397	46
	Br	219 (2,65); 267 (3,69); 286 (4,43); 351 (0,74); 369 (0,74)	396	27	398	28	392	30
 III a-c	H	269 (4,10); 346 (1,48); 370 (1,05)	542	39	540	45	455	37
	OCH_3	280 (3,55); 340 (1,74); 384 (0,84)	542	50	540	52	455	45
	Br	276 (4,46); 347 (1,72); 384 (1,19)	542	30	545	34	457	20

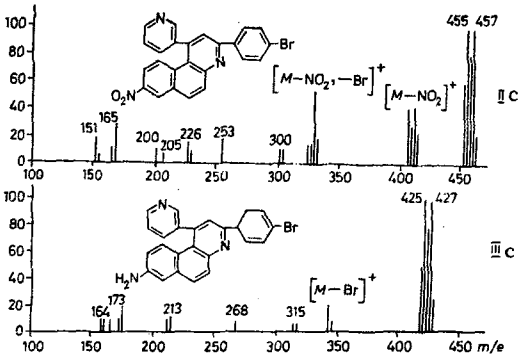


Fig. 1. Mass spectra of IIc and IIIc.

structures for the synthesized compounds. The high intensities of the molecular-ion peaks and the relatively small number of peaks of fragment ions in the mass spectra constitute evidence for the high degree of aromatic character of the investigated compounds.

The principal process in the fragmentation of 8-nitro derivatives of benzo[f]quinoline (II) under the influence of electron impact is elimination of a nitro group from the molecular ion. The $[M - NO]^+$ and $[M - NO, - H]^+$ ion peaks also confirm the presence of a nitro group in IIa-c; their formation is associated with nitro–nitrite rearrangement in the molecular ion.

The configuration of the molecular-ion peaks and the $[M - Br]^+$ ion peak in the mass spectra of IIc and IIIc constitute evidence for the presence of a bromine atom in them.

The electronic absorption spectra of 1-(3-pyridyl)-3-aryl-8-aminobenzo[f]quinolines III lie in the UV region (200-400 nm) (Table 2). Benzo[f]quinolines that do not contain an amino group – 1-(3-pyridyl)-3-aryl-

benzo[f]quinolines A (a-c) – were used as model compounds to study the effect of the amino group on the absorption and luminescence spectra.

The absorption spectra of quinolines A are similar to the spectra of the previously investigated 1,3-diaryl-substituted benzo[f]quinolines [1]. They consist of three bands (Table 2): α band [350 and 367 nm (log ε 3.87)], which has a vibrational structure, and p and β bands [284 and 264 nm (log ε 4.65 and 4.57)]. The introduction of an electron-donor amino group in the 8 position of benzo[f]quinoline leads to a substantial change in the absorption spectrum: As a consequence of drawing together of the p and β bands, one broad band at 270-280 nm is formed. The long-wave band experiences a bathochromic shift with a simultaneous slight increase in the intensity. This is in agreement with the data in [2].

Yet another band at 340-350 nm appears in the absorption spectrum of III. A similar phenomenon has been previously observed [3].

The investigated compounds luminesce well in solution. The fluorescence quantum yields range from 20 to 50%. The fluorescence spectra of model compounds A are structureless and lie in the UV region (λ_{max} ~ 395-407 nm). The Stokesian shift of the fluorescence band is ~30 nm.

The transition from compounds A to 8-amine derivatives III leads to a considerably more pronounced shift of the fluorescence band as compared with the absorption. The Stokesian shift of the fluorescence band increases to 160-170 nm (Table 2). This fact constitutes evidence for intensification of the interaction of the amino derivatives of benzo[f]quinoline with the media in the excited state.

The fluorescence spectra of 8-aminobenzo[f]quinolines III have only one structureless band. The position of the fluorescence maximum and the half-width of the spectrum depend only slightly on the character of substituent R in the phenyl ring (Table 2). However, the energy characteristics of the fluorescence change appreciably. Being a heavy atom, bromine, by changing the probability of the singlet–triplet conversion, decreases the fluorescence quantum yield (Table 2, IIIc). The methoxy group, on the other hand, increases the quantum yield appreciably, in agreement with the literature data [4] and our previous data [1].

In contrast to compounds A, the fluorescence spectra of amino derivatives (III) of benzo[f]quinoline depend substantially on the nature of the solvent. Transition from polar solvents (ethanol and DMSO) to a nonpolar solvent (benzene) leads to a pronounced short-wave shift of the fluorescence spectrum ($\Delta\lambda$ ~ 85 nm), whereas the shift of the long-wave absorption band does not exceed a few nanometers. This significant effect of the solvent on the fluorescence spectra attests to intensification of the interaction of the excited fluorescing molecule with the solvent. The reason for this may be either the formation of a complex with the solvent in the excited state or intensification of the orientation interactions as a consequence of a change in the dipole moment of the fluorescing molecule during excitation. An analysis of the spectral position of the fluorescence band in protic (ethanol) and aprotic (DMSO and benzene) solvents with different polarities indicates that the second mechanism is more likely.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The mass spectra were recorded with a Varian MAT-311 spectrometer with direct introduction of the compounds into the ion source at an ionizing-emission energy of 70 eV. The volatilization temperature was 100°C. 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 Fica-55 absolute spectrofluorimeter. Excitation of the luminescence was accomplished at the long-wave absorption band. The solvents were dry ethanol, DMSO, and benzene. The fluorescence quantum yields were measured by a relative method. A solution of 3-amino-N-methylphthalimide in ethanol was used as the standard.

1-(3-Pyridyl)-3-aryl-8-nitrobenzo[f]quinoline (IIa-c). A mixture of 0.01 mmole of azomethine Ia-c, 0.04 mmole of 3-acetylpyridine, 50 ml of n-butanol, 10 drops of concentrated HCl, and 30 ml of nitrobenzene was heated at a bath temperature of 130-140°C for 30 min, after which it was cooled, and the precipitate was removed by filtration, neutralized with NH_4OH, washed with water, and recrystallized from nitromethane–DMF. An additional amount of II was isolated by evaporation of the mother liquor.

1-(3-Pyridyl)-3-aryl-8-aminobenzo[f]quinoline (IIIa-c). A hot solution of 0.01 mmole of $SnCl_2 \cdot 2H_2O$ in concentrated HCl was added dropwise to a suspension of 0.014 mmole of IIa-c in 80 ml of glacial acetic acid, and the mixture was heated at 100°C for 30 min. It was then cooled, and the precipitate was removed by filtration, neutralized with NH_4OH, washed with water, and dried. Compounds IIIa-c were extracted with toluene in a Soxhlet apparatus.

1-(3-Pyridyl)-3-arylbenzo[f]quinolines A(a-c) were obtained by the method in [5].

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SYNTHESIS OF N-2-PROPYNYL-ω-AMINOALKYL-8-QUINOLINESULFONAMIDES

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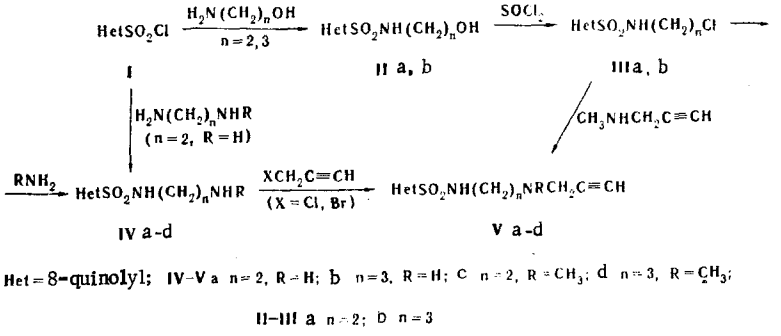
N-2 Propynyl-ω-aminoalkyl-substituted 8-quinolinesulfonamides, which are potential inhibitors of monoaminooxidase, were synthesized by alkylation of ω-aminoalkyl-8-quinolinesulfonamides with propargyl halides or by aminolysis of ω-chloroalkyl-8-quinolinesulfonamides with N-methylpropargylamine.

In connection with the research on the synthesis of inhibitors of monoaminooxidase in the quinoline series – 2-propynylamine derivatives [1, 2] – it seems of interest to obtain quinoline compounds in which heteroatoms (for example, in the form of a sulfonamido group) are also included in the carbon chain to which the 2-propynylamino grouping is attached. We selected quinoline-8-sulfonic acid derivatives for this purpose.

Relatively little study has been devoted to quinoline-8-sulfonamide and its N-substituted derivatives [3-6]. Of the N-(ω-aminoalkyl)quinoline-8-sulfonamides, only the 4-aminobutyl compound has been described [7].

The present communication is devoted to the synthesis of N-2-propynyl-ω-aminoalkyl derivatives of quinoline-8-sulfonamide. The synthesis was accomplished via the scheme:



Het = 8-quinolyl; IV-V a n = 2, R = H; b n = 3, R = H; c n = 2, R = CH_3; d n = 3, R = CH_3;

II-III a n = 2; b n = 3

The reaction of quinoline-8-sulfonyl chloride (I) with the corresponding amino alcohols gave ω-hydroxyalkyl-substituted compounds (IIa, b), which were converted to ω-chloro derivatives (IIIa, b). Ammonolysis or aminolysis of chlorides IIIa, b leads to ω-aminoalkylsulfonamides (IVa-d); the same derivatives (for example,

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