EFFECT OF A PYRIDINE SUBSTITUENT ON SPECTRAL CHARACTERISTICS OF BENZO[f]QUINOLINES WITH AN ANNELATED ALICYCLIC RING

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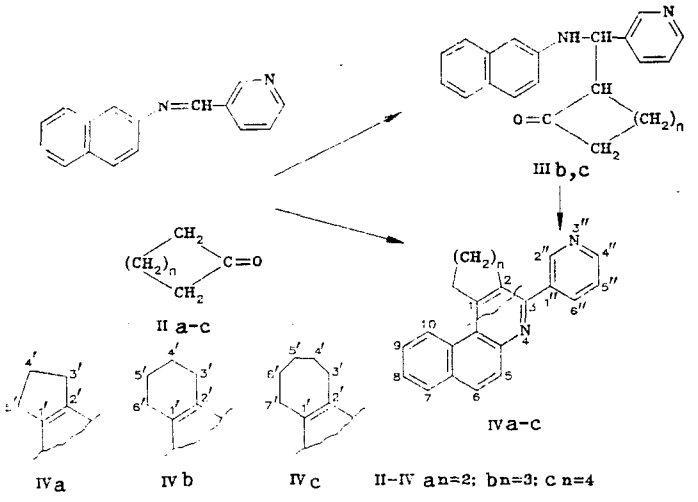
Reaction of N-(2-naphthyl)formimidoyl-3-pyridine with cyclic ketones leads to the formation of 1,2-cycloalkyleno-3-(3-pyridyl)benzo[f]quinolines. Aminoketones, namely, 2-[(3-pyridyl)(2-naphthylamino)methyl]cycloalkanones, are intermediates in this reaction. The absorption-luminescence, PMR, and mass spectra of these newly synthesized compounds have been investigated.

We have previously studied [1, 2] the spectral properties of 3-aryl- and 4-pyridylbenzo-[f]quinolines containing annelated alicyclic rings in the 1,2-position, and found that some of these compounds exhibit intense fluorescence. In continuation of our studies of the effect of structural factors on the spectral luminescence characteristics in this series of benzo[f]-quinoline derivatives, we have investigated the absorption spectra, fluorescence, and fluores cence quantum yield of 1,2-cycloalkylenobenzo[f]quinolines containing a 3-pyridyl substituent in the 3-position (Scheme 1). Compounds IVa-c were prepared by refluxing N-(2-naphthyl)form-imidoyl-3-pyridine (I) with cyclic ketones (cyclopentanone, cyclohexanone, cycloheptanone) IIa-c in the presence of a catalytic amount of conc. HCl for 1-2 h. Under milder reaction conditions (less catalyst, 50°C, 30 min) intermediate reaction products, noncyclic aminoke-tones IIIb, c, were isolated. Heating the latter compounds under harsher conditions (ampul, conc. HCl, nitrobenzene, 120-130°C) led to the formation of the benzoquinoline ring system IV. The physical chemical properties of these newly synthesized compounds are given in Table 1.

Scheme 1



The IR spectra of the aminoketones IIIb,c contain absorption bands in the regions 3405-3250 and 1715-1695 cm^{-1}, which are assigned to stretching vibrations of the NH and CO groups, respectively; stretching bands due to the alicyclic CH_2 groups are also present, at 2945 and 2865 cm^{-1}.

The mass spectra of the benzo[f]quinolines IVa-c contain maximum intensity peaks due to the molecular ions M^+, and almost equal intensity peaks due to $(M - H)^+$ ions. In addition,

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TABLE 1. Physical Chemical Properties of the Newly Synthesized Compounds IIIb,c and IVa-c

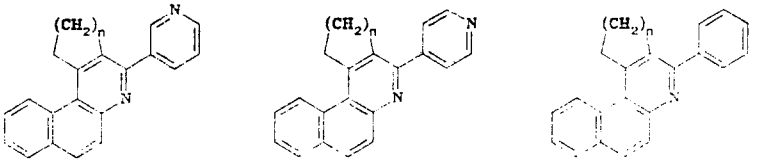
Compound*	Molecular formula	mp, °C	Chemical shift, δ, ppm														Coupling constant, J, Hz					Yield, %
			5-H, d	6-H, d	7-H, m	8-H, 9-H, m	10-H, m	3′-H, m	4′-H, m	5′-H, m	6′-H, m	7′-H, m	2″-H	4″-H	5″-H, dd	6″-H	$J_{5,6}$	$J_{2'',6''}$	$J_{4'',5''}$	$J_{4'',6''}$	$J_{5'',6''}$	
IIIb	$C_{22}H_{22}N_2O$	150...152	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	49
IIIc	$C_{23}H_{24}N_2O$	159...161	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	59
IVa	$C_{21}H_{16}N_2$	154...155	7,97	7,87	7,85	7,57	8,53	3,13	2,14	3,60	—	—	9,07, br.s	8,62, br.d	7,38	8,17, ddd	9,0	1,8	4,6	1,8	8,4	17
IVb	$C_{22}H_{18}N_2$	164...165	7,90	7,72	7,87	7,57	8,67	2,79	1,77		3,48	—	8,81, br.d	8,64, dd	7,36	7,85, ddd	9,1	2,2	4,8	1,6	8,9	42
IVc	$C_{23}H_{20}N_2$	181...185	7,82	7,79	7,85	7,55	8,38	2,95	1,82...2,06			3,47	8,78, br.s	8,62, br.d	7,38	7,91, br.d	9,0	—	4,3	—	8,4	38

*For atom numbering, see Scheme 1.

just as in the spectra of the previously studied [2] 1,2-cycloalkyleno-3-(4-pyridyl)benzo[f]-quinolines, there are also medium intensity peaks due to $(M - H, -C_5H_4N)^+$ ions, arising via elimination of the pyridine substituents from the $(M - H)^+$ ions. The presence of doubly charged M^{2+} ion peaks is also characteristic of condensed heteroaromatic compounds. The aminoketones IIIb,c were found to be less stable with respect to electron impact than the benzo-[f]quinoline derivatives. The most intense peak in the spectra of compounds IIIb,c is at m/e 233, resulting from cleavage of the cycloalkanone substituent from the molecular ion. All of the compounds also exhibit low intensity peaks corresponding to cleavage of the cycloalkane ring.

In the PMR spectra (Table 1) of the cyclic products IVa-c the number and position of the signals, their multiplicity and coupling constant values, correctly reflect the proposed structures of the substances. In the case of compound IVb the signals due to the cyclohexane ring protons appear as multiplets at 1.77, 2.79, and 3.48 ppm. The most characteristic feature of the spectra of these compounds is the presence of doublets at 7.72 and 7.90 ppm (J = 9.1 Hz), which confirms the angular structure of the benzo[f]quinoline ring. The positions of the other signals due to the aromatic protons in the benzoquinoline ring and in the pyridine substituent are analogous to their assignments in the spectrum of 1-aryl-3-(3-pyridyl)-benzo[f]quinoline [3], with the exception of the 10-H and 9-H signal positions, which are shifted substantially downfield ($\Delta\delta$ = 1.0 for 10-H and $\Delta\delta$ = 0.4 ppm for 9-H); this effect is attributed to the magnetic anisotropy of the C—C bonds in the annelated alicyclic rings. A significant upfield shift of the proton signals for the pyridine substituent ($\Delta\delta$ = 0.6 for 2"-H and $\Delta\delta$ = 0.65 ppm for 6"-H) is also observed, apparently due to the possibility of rotation of the pyridine substituent within the molecular plane in such a way that the pyridine ring proton closest to the alicyclic ring diverges from the so-called deshielding cone of the alicyclic C—C bonds. The roughly equal effect on the 2"-H and 6"-H protons in the pyridine substituent can be explained in terms of the existence of conformational isomers, which can be interconverted via rotation about the $C_{(3)}$—$C_{(1")}$ single bond. In the PMR spectrum of aminoketone IIIc the singlets due to the amino proton at 6.57 ppm and the methine proton at 5.04 ppm appear broadened. The methylene protons in the cycloheptane ring give rise to a series of multiplets in the range 1.18-3.28 ppm. The aromatic proton signals appear in the range 6.80-8.87 ppm, with several of the signals consisting of two sets of peaks (with an integrated intensity ratio of 1:2) due to the presence of two diastereomers for this compound.

The UV absorpton spectra of compounds IVa-c (Table 2) exhibit the structure typical of benzo[f]quinolines [4, 5]. Replacement of the aryl radical in 1,2-cycloalkyleno-3-arylbenzo-[f]quinolines VIa-c by a 3-pyridine substituent in compounds IVa-c produces an insubstantial bathochromic shift of the β- and p-bands and increases their intensity, and at the same time leads to a weak hypsochromic shift of the α-band. The α-band retains its well resolved vibrational fine structure. Comparison of the absorption spectra of compounds IVa-c with the spectra of the previously synthesized 1,2-cycloalkyleno-3-(4-pyridyl)benzo[f]quinolines Va-c [2] reveals the following difference in the region of the β-band: disappearance of the maximum at 235 nm in the 3-pyridylbenzo[f]quinolines. Enhanced intenity of the p- and α-absorption bands is also observed in the case of compounds containing annelated six- and seven-membered rings.



IVa-c V a-c VI a-c

IV-VIa n=2; b n=3; c n=4

The fluorescence spectra of the 3-pyridylbenzo[f]quinolines IVa-c occur in the 350-450 nm region. The values of the Stokes shift are approximately 30 nm. The spectra of compounds IVb,c are unstructured, while the fluorescence of compound IVa is sharply structured in all of the solvents investigated. The (fine) structure also appears in the luminescence spectrum of 1,2-cyclophenyleno-3-(4-pyridyl)benzo[f]quinoline (IVa) in benzene solution (Table 2). This observation is indicative of a high degree of coplanarity in these compounds. Quantum mechanical calculations, carried out by us for the related compound 1-phenyl-3-(4-pyridyl)-benzo[f]quinoline using the semi-empirical CNDO MO approximation, confirm this hypothesis. As

TABLE 2. Spectral Luminescence Characteristics of Benzo[f]-quinoline Derivatives IV-VI

Compound	Absorption (ethanol), λ_{max}, nm (log ε)	Fluorescence, λ_{max}, nm (η, %)		
		benzene	ethanol	DMSO
IVa	218 (4,07), 262 (4,34), 325 (3,17), 341 (3,37), 356 (3,40)	372, 390 (20)	372, 390 (27)	373, 390 (27)
IVb	221 (4,21), 258 (4,46), 323 (3,25), 338 (3,42), 353 (3,46)	382 (3)	385 (6)	382 (5)
IVc	217 (4,41), 262 (4,66), 325 (3,47), 341 (3,67), 356 (3,73)	378 (8)	385 (12)	382 (9)
Va	222 (4,60), 237 (4,25), 269 (4,53), 322 (3,30), 344 (3,49), 358 (3,51)	378, 394 (11)	395 (17)	395 (15)
Vb	221 (4,17), 238 (4,20), 258 (4,39), 322 (3,12), 335 (3,30), 350 (3,34)	390 (3)	400 (7)	400 (5)
Vc	220 (4,41), 237 (4,34), 267 (4,61), 325 (3,36), 340 (3,57), 355 (3,62)	390 (5)	400 (6)	400 (10)
VIa	260 (4,46), 342 (3,46), 360 (3,52)	—	370, 386 (49)	—
VIb	258 (4,19), 322 (3,00), 338 (3,14), 354 (3,20)	—	370, 384 (7)	—
VIc	260 (4,58), 320 (3,50), 342 (3,78), 357 (3,85)	—	373, 385 (13)	—

can be seen from the data in Table 2, introduction of a nitrogen atom into the aryl substituent decreases the luminescence efficiency. The fluorescence quantum yields η for compounds IVa-c are in the range 3-25%. The highest quantum yield is observed for benzoquinoline IVa, which contains a strained five-membered ring; a maximum conjugation effect is observed in this compound due to the orientation of four carbon atoms in a single plane. In addition, as noted above, the pyridine substituent also lies in the plane of the molecule. In the case of the less strained six- and seven-membered ring derivatives steric effects begin to be substantial, becoming stronger with increasing ring size [6]. As might be expected, the position of the nitrogen atom in the pyridine substituent affects the luminescence reactivity of these compounds. The fluorescence quantum yields for the 3-pyridylbenzo[f]quinoline derivatives IVa-c are substantially higher than those measured previously for the 4-pyridylbenzo-[f]quinolines Va-c (Table 2). This is related apparently to greater involvement of participation of the π-electrons in the 3-pyridine substituent in the conjugation system of the benzoquinoline molecule [7].

Solvent polarity has almost no effect on the spectral position of the absorpton of fluoresence bands. This suggests that the symmetry of the electronic environment or cloud of these molecules is unchanged upon excitation. The nature of the solvent does, however, have a significant effect on the fluorescence efficiency of these compounds. The highest fluorescence quantum yields are observed in ethanol solution, where hydrogen bonding between the solvent and the heterocyclic nitrogen atom reduces the energy level of the η-electrons and also diminishes the effect of the nonbonded electrons on the nitrogen atom on the π-cloud of the molecule; as a result of these effects, the probability of interconversion is decreased [8]. In aprotic solvents (DMSO, benzene) lower luminescence quantum yields are observed, due to vibrational spin-spin interaction between the $s_{n\pi^*}$ and $s_{\pi\pi^*}$-state, with subsequent interconversion to a triplet level or state. The luminescence quantum yields are, as expected, higher in DMSO than in benzene solutions: the greater viscosity of DMSO facilitates stabilization of the fluorescing molecules [9].

EXPERIMENTAL

IR spectra were recorded on a UR-20 spectrophotometer using KBr pellets; UV spectra were measured on a Specord UV-Vis spectrophotometer using ethanol solutions. PMR spectra were obtained on a Bruker WM-360 spectrometer at an operating frequency of 360 MHz, using 10% solutions in $CDCl_3$ versus TMS as internal standard. Mass spectra were measured on a Varian MAT-311 spectrometer using direct introduction of the sample into the ion source at an ionizing electron energy of 70 eV. The vaporization temperature was 100°C. The results of C, H, N elemental analysis for compounds III and IV agreed with the calculated values.

N-(2-Naphthyl)formimidoyl-3-pyridine was prepared according to [3].

1,2-Cycloalkyleno-3-(3-pyridyl)benzo[f]quinoline (IVb). A mixture of 2.32 g (10 mmoles) compound I, 1.47 g (15 mmoles) cyclohexanone, 20 ml butanol, and 0.64 ml conc. HCl was heated

for 1 h at 50°C, and then an additional 1 h at 120-130°C. The mixture was cooled and the resulting precipitate was removed by filtration, neutralized with 25% aqueous NH_4OH solution, and washed with water to neutral pH. The material was crystallized from isopropyl alcohol to give 1.30 g (42%) of compound VIb.

Benzo[f]quinolines (IVa,c) were prepared in an analogous manner.

2-[(3-Pyridyl)(2-naphthylamino)methyl]cyclohexanone (IIIb). A mixture of 2.32 g (10 mmoles) azomethine I, 1.47 g (15 mmoles) cyclohexanone, 20 ml isopropyl alcohol, and 0.16 ml conc. HCl was heated for 20 min at 50°C. After solvent evaporation the residue was treated with 70 ml ether to remove resinous materials, then neutralized with 25% aqueous NH_4OH solution and washed with water to a neutral reaction point. Yield 1.60 g (49%) of aminoketone IIIb (from a mixture of isopropyl alcohol–benzene, 2:1).

Aminoketone (IIIc) was prepared similarly.

Cyclization of 2-[(3-Pyridyl)(2-naphthylamino)methyl]cyclohexanone. A mixture of 1.0 g (3.3 mmoles) compound IIIb, 20 ml butanol, 0.4 ml conc. HCl, and 1 ml nitrobenzene was heated for 2 h in an ampul at 150°C. The mixture was cooled and the resulting precipitate was removed by filtration, neutralized with 25% aqueous NH_4OH, and washed with water to a neutral reaction point. Yield 0.62 g (66%) of benzo[f]quinoline IVb (from isopropyl alcohol).

Cyclization of aminoketone IIIc to benzo[f]quinoline IVc was carried out in an analogous manner.

LITERATURE CITED

1. N. S. Kozlov, L. F. Gladchenko, V. A. Serzhanina, G. V. Vobor'eva, O. D. Zhikhareva, and R. D. Sauts, Khim. Geterotsikl. Soedin., No. 9, 1237 (1977).
2. N. S. Kozlov, S. V. Mikhalevskyaa, L. F. Gladchenko, and V. A. Serzhanina, Khim. Geterotsikl. Soedin., No. 7, 947 (1986).
3. N. S. Kozlov, S. V. Mikhalevskaya, and V. A. Serzhanina, Khim. Geterotsikl. Soedin., No. 3, 351 (1989).
4. N. S. Kozlov, L. F. Gladchenko, R. D. Sauts, and V. A. Serzhanina, Khim. Geterotsikl. Soedin., No. 12, 1646 (1978).
5. V. A. Serzhanina, R. D. Sauts, L. F. Gladchenko, and N. S. Kozlov, Khim. Geterotsikl. No. 8, 1092 (1987).
6. K. Blaga, O. Chervinka, and Ya. Kovar, Principles of Stereochemistry and Conformational Analysis [in Russian], Khimiya, Leningrad (1974).
7. J. Joule and H. Smith, Principles of the Chemistry of Heterocyclic Compounds [Russian translation], Mir, Moscow (1975).
8. B. M. Krasovitskii and B. M. Bolotin, Organic Luminophors [in Russian], Khimiya, Moscow (1984).
9. N. S. Kozlov, L. F. Gladchenko, V. A. Serzhanina, G. S. Shmanai, I. P. Stremok, and G. P. Korotysheva, Khim. Geterotsikl. Soedin., No. 4, 511 (1978).