SYNTHESIS AND LUMINESCENCE OF BENZO[f]QUINOLINE DERIVATIVES WITH FUSED ALICYCLIC RINGS

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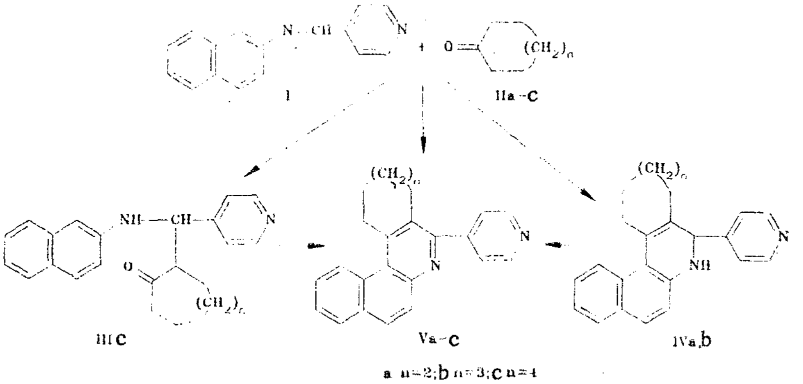
Cyclic ketones react with N-(2-naphthyl)formimidoyl-4-pyridine in refluxing aliphatic alcohol to form 1,2-(1',2'-cycloalkylene)-3-(4-pyridyl)benzo[f]quinolines. Under mild conditions, cyclopentanone and cyclohexanone gave dihydrobenzo[f]quinoline derivatives — 1,2-(1',2'-cycloalkylene)-3-(4-pyridyl)-3,4-dihydrobenzo[f]-quinolines, whereas cycloheptanone gave an aminoketone — 2-[(4-pyridyl)(2-naphthylamino)methyl]cycloheptanone.

Derivatives of benzo[f]quinoline containing 1,2-fused alicyclic rings fluoresce strongly [1]. As part of an investigation of this type of luminophore, the 1,2-cycloalkylene derivatives of benzo[f]quinoline (III-V) were prepared by reacting N-(2-naphthyl)formimidoyl-4-pyridine (I) with a cyclic ketone (II) in the presence of mineral acid; the luminescent properties (absorption spectra, fluorescence, fluorescence quantum yield) of these derivatives was examined.



On refluxing the starting compounds in an aliphatic (C_2—C_4) alcohol for times ranging from 15 min to 2 h, all the ketones (cyclopentanone, cyclohexanone, and cycloheptanone) gave the corresponding benzo[f]quinolines — 1,2-(1',2'-cycloalkylene)-3-(4-pyridyl)benzo[f]quinoline (Va-c). Under mild conditions (50°, 30 min to 1 h reaction time), cyclopentanone and cyclohexanone formed dihydroderivatives — 1,2(1',2'-cycloalkylene)-3-(4-pyridyl)-3,4-dihydrobenzo[f]quinoline (IVa and b), and cycloheptanone gave the aminoketone IIIc — 2-[(4-pyridyl)-(2-naphthylaminomethyl]cyclopheptanone (Table 1). The structures of these compounds were confirmed by spectral data and also by the conversion of the intermediates IIIc and IVa and b to the corresponding benzo[f]quinoline Va-c by refluxing in alcohol in the presence of a catalyst and an oxidizing agent.

Bands at 3380, 1690, and 3300 cm^{-1} in the infrared spectra of the aminoketone III and the dihydrobenzo[f]quinolines IV, and stretching and deformation vibrations from the benzo[f]-quinoline ring in the spectrum of compound V [2], confirmed the structures of these compounds. Mass-spectral data on the benzo[f]quinolines V showed that these compounds were stable to the action of electron bombardment. The strongest peak was that of the molecular ion M$^+$; there

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TABLE 1. Physicochemical Data

Compound	n	mp,*	IR spectrum, cm^{-1}	Found, %			Empirical formula	Calculated, %			Yield, %
				C	H	N		C	H	N	
IIIc	4	146—148	3380(ν_{NH}), 1525(δ_{NH}), 1690(ν_{CO})	80,2	7,0	8,0	$C_{23}H_{24}N_2O$	80,2	7,0	8,1	44,0
IVa	2	230—232	3300(ν_{NH}), 1525(δ_{NH})	84,2	6,4	9,0	$C_{21}H_{18}N_2$	84,5	6,1	9,4	13,4
IVb	3	236—238	3300(ν_{NH}), 1525(δ_{NH})	84,5	6,6	8,9	$C_{22}H_{20}N_2$	84,6	6,5	9,0	21,2
Va	2	170—172	3050, 3030(ν_{CH} arom.); 2960, 2850(ν_{CH_2}); 1600, 1560, 1485, 1445($\nu_{C=C}$); 835, 760(δ_{CH} shoulder.)	85,0	5,6	9,4	$C_{22}H_{18}N_2$	85,1	5,4	9,5	27,0
Vb	3	162—163	3060, 3030(ν_{CH} arom.); 2960, 2860(ν_{CH_2}); 1600, 1550, 1480, 1435($\nu_{C=C}$); 835, 760(δ_{CH} shoulder.)	84,9	5,9	8,9	$C_{22}H_{18}N_2$	85,1	5,9	9,0	25,7
Vc	4	176—177	3050, 3010(ν_{CH} arom); 2920, 2860(ν_{CH_2}); 1600, 1560, 1480, 1440($\nu_{C=C}$); 835, 760(δ_{CH} shoulder.)	85,0	6,3	8,5	$C_{23}H_{20}N_2$	85,2	6,2	8,6	26,7

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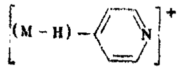
*Compounds IIIc and Va-c were recrystallized from isopropanol, and IVa and b from a mixture of isopropanol and toluene.

was also an $(M - H)^+$ peak. In the mass spectra of the dihydro derivatives of benzo(f)quinoline IV along with the molecular ion peak M^+ there are low-intensity peaks $(M - 2H)^+$, formed as a result of aromatization of the dihydro derivatives IV a and b to the corresponding benzo(f) quinolines V a and b by the action of electron bombardment. In the mass spectrum of Iv a there is also the peak



The ultraviolet spectra of the benzo [f]quinolines V exhibit three bands, due to electron transitions in the benzene and pyridine rings: high-intensity β-bands (258-269 nm; log ε 4.39-4.61), p-(293-325 nm; log ε 4.19-3.12) and α-bands with weak vibrational structures (335-344 and 350-358 nm; log ε 3.30-3.57 and 3.34-3.62 nm). Comparison of the absorption spectrum of compound V with the spectrum of 1,2-(1'2'-cycloalkylene)-3-arylbenzo[f]quinoline [1] showed that the introduction of a pyridyl group at position 3 led to a bathochromic shift of the β- and p-bands, and a hyperchromic effect for the β-bands. Compound V fluoresces in the UV (390-400 nm); the Stokes shift is 40-50 nm. The fluorescence spectra of V are structureless in the solvent used, except that in benzene, compound Va, which has a five-membered alicyclic ring, gives rise to two maxima (Table 2). The fluorescence quantum yields are low and range from 3-17%. The decrease in the fluorescence quantum yield in comparison with compounds such as 1,2-(1',2'-cycloalkylene)-3-arylbenzo[f]quinoline [1] is apparently due to destruction of the coplanarity of the benzo[f]quinoline molecule when the phenyl group at 3 position is replaced by a pyridyl group. Benzo[f]quinoline has the highest quantum yield; this compound has a strained five-membered ring — the four carbon atoms are in one plane, producing the maximum hyperconjugation effect. In the less strained six- and seven-membered rings (compounds Vb and c) the steric effect, which increases with ring size, becomes more important [3]. The position of the fluorescence band shows a weak dependence on the nature of the solvent, indicating the stability of the dipole moment of the molecule on excitation [4]. The maximum fluorescence quantum yield (17%) was observed with ethanol where hydrogen bonding between the nitrogen atom and the solvent reduces the influence of the free electrons in the π-electron cloud and consequently also the probability of interconversion [5].

On going to the partially hydrogenated derivatives of benzo[f]quinoline, the unshared electrons on the nitrogen atom are lost to the conjugation system, and this shows up in the luminescent properties of these compounds (Table 2). The absorption spectra of compounds IVa and b are analogous to those of 2-naphthylamine and contain bands corresponding to π—π*

TABLE 2. Luminescence Data for Benzo[f]quinoline Derivatives

Compound	n	Absorption (ethanol), λ_{max}, nm(log ε)	Fluorescence, λ_{max} (γ, %)		
			benzene	ethanol	DMSO
IVa	2	257 (4,64), 303 (3,87), 315 (3,78), 370 (3,63)	428 (25)	440 (4)	448 (42)
IVb	3	257 (4,70), 298 (3,96), 310 (3,88), 370 (3,65)	408,425 (25)	did not luminesce	437 (36)
Va	2	269 (4,53), 293 (4,19), 3,44 (3,49), 358 (3,51)	378,394 (11)	395 (17)	395 (15)
Vb	3	258 (4,39), 322 (3,12), 335 (3,30), 350 (3,34)	390 (3)	400 (7)	400 (5)
Vc	4	267 (4,61), 325 (3,36), 340 (3,57), 355 (3,62)	390 (5)	400 (6)	400 (10)

type transitions; there is a bathochromic shift compared with bands of 2-naphthylamine [6]. The dihydro derivatives IVa and b luminesce fairly strongly in aprotic solvents (25-42% in benzene and DMSO), but show almost no luminescence in ethanolic solution. Quenching of the fluorescence in ethanol is apparently due to the protonation of the nitrogen atom of the pyridine ring. This is supported by the observation that there is no significant change in the position of the fluorescence bands (425-440 nm) on going from aprotic to protic solvents. The higher luminescence quantum yield in DMSO compared with benzene can be explained by the increase in viscosity of the solvent, which helps to stabilize the fluorescing molecule [7].

EXPERIMENTAL

Infrared spectra were taken on a UR-20 instrument; samples were measured in KBr pellets. UV spectra were measured on a Specord UV-vis; samples were dissolved in ehtanol (10^{-4} mole/liter). Mass spectra were recorded on a Varian MAT-311 with direct introduction of the sample into the ion source at an ionization energy of 70 V. Vaporization temperature was 100-180°C. Fluorescence spectra and the absolute fluorescence quantum yields were measured on an SLM-4800 spectrofluorimeter. Excitation of fluorescence was carried out at a wavelength of 350 nm, the long-wave absorption region for the solutions examined. The absolute fluorescence quantum yield was calculated by the relative method. The solvents used were dry ethanol, benzene, and DMSO. A solution of 3-amino-N-methylthalimide in absolute ethanol was used as a standard. The compounds were examined by TLC on Silufol UV-254 plates (eluent, carbon tetrachloride—ethanol—acetic acid, 10:1:1; visualization in UV light).

N-(2-Naphthyl)formimidoyl-4-pyridine (I) was prepared by the method given in [8].

1,2-(1',2'-Cyclohexylene)-3-(4-pyridyl)-3,4-dihydrobenzo[f]quinoline (IVb) and 1,2-(1',2'-cyclohexylene)-3-(4-pyridyl)benzo[f]quinoline (Vb). A mixture of 2.32 g (10 mmole) of compound I, 1.47g (15 mmole) of cyclohexanone, 20 ml of isopropanol, and 10 drops of concentrated HCl was heated at 50° for 1 h, then at 80-85° for a further 1 h. The mixture was cooled and the precipitated material was filtered off, neutralized with 25% ammonium hydroxide, and washed with water until the washings were neutral. Recrystallization from a 1:1 mixture of isopropanol and toluene gave 0.66 g (21.2%) of compound IVb. The mother liquors were partially evaporated, and the precipitate filtered and worked up as for IVb to give 0.8 g (25.8%) of compound Vb (from isopropanol). Compounds IVa and Va and b were obtained in the same way.

2-[(4-Pyridyl)(2-naphthylamino)methyl]cycloheptanone (IIIc). A mixture of 2.32 g (10 mmole) of compound I, 1.4 g (12.5 mmole) of cycloheptanone, 20 ml of isopropanol, and 16 drops of concentrated HCl was heated at 50°C for 1 h. After evaporation of the solvent, the residue was treated with 50 ml of ether to extract tarry material, neutralized with 25% ammonium hydroxide, and washed with water until the washings gave a neutral reaction to give 0.76 g (44%) of compound IIIc (from isopropanol).

Cyclization of 2-[(4-pyridyl)(2-naphthylamino)methyl]cycloheptanone. A mixture of 1.0 g (2.9 mmole) of compound IIIc, 1 ml of boron trifluoride etherate, and 20 ml of dry benzene was heated for 1 h on a boiling water bath. After cooling, the rarry materials was separated and treated with 25% ammonium hydroxide, and then washed with water until the washings were neutral; yield 0.65 g (69.1%) of compound Vc (from isopropanol).

Cyclization of 1,2-(1',2'-cyclohexylen)-3-(4-pyridyl)-3,4-dihydrobenzo[f]quinoline. A mixture of 1.0 g (3.2 mmole) of compound IIIb, 20 ml of isopropanol, 10 drops of concentrated HCl, and 1 ml of nitrobenzene was heated in sealed tube for 1 h at 150°C. The mixture was cooled, and the precipitate which separated filtered, neutralized with 25% ammonium hydroxide, and washed with water until the washings gave a neutral reaction. A yield of 0.9 g (87.2%) of compound Vb was obtained.

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