LUMINESCENCE OF DIHYDRO DERIVATIVES OF BENZO[f]QUINOLINE

N. S. Kozlov, L. F. Gladchenko,
G. V. Vorob'eva, V. A. Serzhanina,
and R. D. Sauts

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The spectral luminescence properties of 3-aryl-3,4-dihydrobenzo[f]quinolines containing alicycles and ester groups in the 1 and 2 positions were investigated. It is shown that compounds of this type have intense luminescence (52-76%). The quenching effect of an ester group in the heterocyclic ring was established. The spectral luminescence characteristics of compounds with an ester group in the alicycle are determined by the proton-acceptor properties of the carbonyl function of this group. The effect of the solvent on the spectral luminescence characteristics of the investigated compounds is discussed.

It is known that many benzo[f]quinoline derivatives fluoresce intensely and that the maximum fluorescence quantum yields are observed in alcohol solutions, in which the hydrogen bond of the nitrogen atom of the heteroring with the solvent decreases the effect of the unbounded electrons on the π-electron cloud of the molecule [1, 2].

Transition to partially hydrogenated benzo[f]quinoline derivatives leads to disconnection of the unshared electrons of the nitrogen atom from the conjugation chain, and this should inevitably affect the spectral luminescence characteristics of compounds of this type.

The aim of the present research was to investigate the spectral characteristics of hydrogenated benzo[f]quinoline derivatives containing various substituents in the 1 and 2 positions and to study the effect of a solvent on the spectra and fluorescence quantum yields.

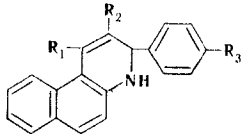
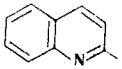
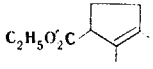
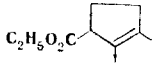
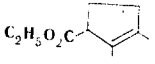
Three intense bands corresponding to transitions between states of the $\pi-\pi^*$ type of the aromatic rings can be isolated in the absorption spectra of dihydro derivatives of benzo[f]quinoline. The absorption band at 290-320 nm in the spectra of compounds containing alicyclic hydrocarbons condensed in the 1 and 2 positions has two maxima of approximately equal intensity (III-V) (Table 1). The incorporation of an ester group in the molecule leads to smoothing out of the structure, a shortwave shift, and an increase in the intensity of the indicated absorption band. The long-wave absorption band experiences a bathochromic shift ($\Delta\lambda \approx 30$ nm) in this case.

Most of the dihydro derivatives of benzo[f]quinoline that we investigated fluoresce intensely. Removal of the unshared electrons of the nitrogen atom from the conjugation chain promotes intense fluorescence in both protic (ethanol) and aprotic [benzene, dimethyl sulfoxide (DMSO)] solvents (III-V). Their luminescence properties are affected by an ester group *I, II, VI-VIII). Practically no fluorescence is observed for compounds with an ester group in the 2 position (I, II). The decrease in the fluorescence intensity of these compounds may be due to either the quenching effect of the electron-acceptor ester group in conjugation with the ring of the molecule or to its twisting vibrations, which may lead to degradation of the electronic excitation energy [3]. The bright fluorescence of crystalline I and II and the kindling of fluorescence of alcohol solutions of them as the temperature is lowered evidently constitute evidence in favor of the second hypothesis.

Compounds VI-VIII, which contain an ester group in the condensed alicycle, fluoresce intensely, and their luminescence characteristics are determined by the proton-acceptor

Institute of Physical Organic Chemistry, Academy of Sciences of the Belorussian SSR. Institute of Physics, Academy of Sciences of the Belorussian SSR, Minsk 220603. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 810-813, June, 1977. Original article submitted June 22, 1976.

TABLE 1. Spectral Luminescence Properties of 3,4-Dihydrobenzo[f]quinoline Derivatives

Compound				Absorption			Luminescence					
				λ_{max}, nm ($\varepsilon \cdot 10^{-4}$), ethanol	λ^*_{max}, nm		ethanol		DMSO		benzene	
	R_1	R_2	R_3		DMSO	benzene	λ_{max}, nm	η, %	λ_{max}, nm	η, %	λ_{max}, nm	η, %
I	CH_3	$CO_2C_2H_5$	OCH_3	245 (3,16), 276 (2,46), 412 (0,59)	—	—	530	<1	—	—	455	<1
II		$CO_2C_2H_5$	H	239 (3,92), 255 (4,04), 366 (1,14)	—	—	495	<1	—	—	—	—
III			H	266 (4,74), 294 (0,85), 304 (0,89), 380 (0,60)	386	376	440	42	453	76	436	54
IV			OCH_3	265 (4,65), 292 (0,75), 304 (0,80), 380 (0,46)	—	—	442	41	453	76	437	53
V			H	266 (4,05), 304 (0,90), 314 (0,74), 374 (0,46)	383	372	432	40	436	71	413, 429	52
VI			H	248 (2,99), 278 (1,88), 409 (0,50)	412	398	530	7	500	67	465	66
VII			OCH_3	248 (4,14), 276 (2,46), 408 (0,62)	412	398	530	5	500	65	465	69
VIII			Cl	248 (3,72), 275 (2,06), 408 (0,59)	410	396	527	6	500	64	465	66

*This is the position of the maxima of the long-wave absorption bands.

properties of the carbonyl function of this grouping. The indicated compounds have high fluorescence quantum yields in aprotic solvents (benzene and DMSO) and fluoresce weakly in ethanol, which is capable of forming a hydrogen bond with the ester carbonyl group. The formation of a charge-transfer complex (CTC) in the excited state in alcohol solutions leads to emissionless deactivation of the electronic excitation [4].

As seen in Table 1, substituents (p-OCH , p-Cl) in the phenyl ring do not affect the luminescence properties of the investigated compounds. This can evidently be explained by the fact that the phenyl ring is not included in the overall conjugation chain.

The presence and position of an ester group in the investigated compounds affect the character of their interaction with the solvent molecules. In the case of III-V, which do not contain an ester group, the position of the spectra depends only slightly on the polarity of the solvent. Transition from benzene ($\mu = 0$) to ethanol ($\mu = 1.7$ D) and DMSO ($\mu = 3.9$ D) leads to a small bathochromic shift of the absorption and fluorescence spectra (Table 1). The small difference in the shifts of the absorption and fluorescence spectra as the polarity of the solvent changes constitutes evidence that the dipole moment of their molecules changes only slightly during excitation [5].

In the case of I and VI-VIII, which contain an ester group, transition from a polar protic (ethanol) to a neutral (benzene) solvent leads to a considerable hypsochromic shift of the fluorescence spectra ($\Delta\lambda_{fl} = -65$ nm). Negative solvatochromism is manifested more weakly in the absorption spectra in this case ($\Delta\lambda_{abs} = -14$ nm). This fact constitutes evidence that the solvent has an additional effect on the excited fluorescing molecule. Two mechanisms are possible for this phenomenon: the formation of a complex with the solvent in the excited state and a change in the orientation interactions that is related to the change in the dipole moment during excitation. Both of the indicated factors evidently contribute to the additional shift of the fluorescence spectra. The formation of a proton-transfer complex in the excited state leads, as a rule, to a bathochromic shift of the fluorescence spectrum [6]. Because of this, the fluorescence spectra of VI-VIII in ethanol, which forms a hydrogen bond with the ester carbonyl group, lie in the longer-wavelength region than in the more polar DMSO; this is not observed for compounds that do not contain an ester group (III-V). The fact that in aprotic solvents with differing polarities (DMSO and benzene) the fluorescence spectra of VI-VIII are shifted relative to one another by 35 nm when $\Delta\lambda_{abs} = 14$ nm constitutes evidence for a change in the orientation interactions in the excited state that is associated with a change in the dipole moment of the molecule. This is also confirmed by the shortwave shift of the fluorescence spectra of the indicated compounds in polar solvents as the temperature is lowered.

EXPERIMENTAL

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. Luminescence excitation was accomplished in 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. The synthesis of III-V was described in [7], and the synthesis of VI-VIII was described in [8].

Ethyl 1-Methyl-3-(p-methoxyphenyl)-3,4-dihydrobenzo[f]quinoline-2-carboxylate (I). Five drops of concentrated HCl were added to a heated (to 70°) solution of 2.61 g (10 mmole) of p-methoxybenzylidene-2-naphthylamine and 5.2 g (40 mmole) of acetoacetic ester in 25 ml of ethanol, and the solution was cooled, neutralized with NH_4OH, and filtered to give 1.4 g (38%) of ester I with mp 154-155° (ethanol). Found: C 77.6; H 6.2; N 3.9%. $C_{24}H_{23}NO_3$. Calculated: C 77.8; H 6.2; N 3.8%. IR spectrum (KBr): 1700 (ester OC) and 3365 cm^{-1} (NH).

Ethyl 1-(2-Quinolyl)-3-phenyl-3,4-dihydrobenzo[f]quinoline-2-carboxylate (II). A mixture of 0.57 g (2.5 mmole) of benzylidene-2-naphthylamine, 0.65 g (2.5 mmole) of quinaldinoylacetic ester, 3 ml of dimethylformamide, and two drops of concentrated HCl was heated at 100° for 15 min, after which it was evaporated to dryness, and the resinous residue was neutralized with NH_4OH and treated with petroleum ether and diethyl ether to give 0.7 g (63%) of ester II with mp 119-120° (ethanol). Found: C 81.2; H 5.1; H 6.0%. $C_{31}H_{24}N_2O_2$. Calculated: C 81.6; H 5.3; N 6.1%. IR spectrum: (KBr): 1683 (ester C=O) and 3400 cm^{-1} (NH).

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POLYMETHYL-SUBSTITUTED 2-AZAFLUORENES AND SYNTHESIS OF AZAFLUORANTHENE DERIVATIVES FROM THEM

N. S. Prostakov, A. A. Obynochnyi, V. V. Dorogov, V. P. Zvolinskii, V. F. Zakharov, and A. A. Savina

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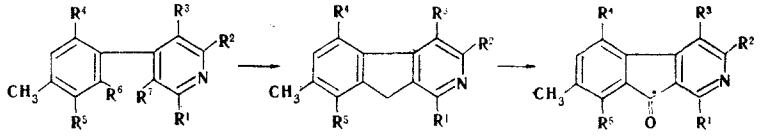
It was established that polymethyl-substituted 2-azafluorenes obtained by catalytic dehydrocyclization of pyridine- and benzene-ring-substituted γ-arylpyridines have different structures depending on the position of the methyl groups in the starting compound and which methyl group participates in the cyclization reaction. The 1,4,7-trimethyl-2-azafluorene synthesized by this method was used for the preparation of new condensed heterocyclic systems of the 3-azafluoranthene and cyclohexano-8-azafluoranthene type.

2-Azafluorenes were obtained by the method described in [1] by dehydrocyclization of γ-arylpyridines containing a methyl group in the β position of the pyridine ring. In the case of β-methyl-γ-phenylpyridine this reaction proceeds unambiguously to give 2-azafluorene. We have demonstrated in the present research that dehydrocyclization of the analogous pyridine bases with one or several methyl groups in the benzene ring may proceed with the participation of different methyl groups.

We studied the compounds formed by dehydrocyclization of the following pyridine bases on a K-16 catalyst at 560-580°C: 2,5-dimethyl-4-(3,4-dimethylphenyl)- (I), 2,5-dimethyl-4-(2,4,5-trimethylphenyl)- (II), and 2,5-dimethyl-4-(2,4,6-trimethylphenyl)pyridine (III), as well as 2,5-dimethyl-4-(2,4-dimethylphenyl)pyridine (IV), the dehydrocyclization of which was described in [2]. The polymethyl-substituted 2-azafluorenes were isolated in up to 20% yields.



I-IV V-VIII IX-XII

I $R^1=R^3=R^4=R^6=H$, $R^2=R^5=R^7=CH_3$; II $R^1=R^3=R^6=H$, $R^2=R^4=R^5=R^7=CH_3$; III $R^1=R^3=R^5=H$, $R^2=R^4=R^6=R^7=CH_3$; IV $R^2=R^4=R^5=R^7=H$, $R^1=R^3=R^6=CH_3$; V, IX $R^1=R^3=R^4=H$, $R^2=R^5=CH_3$; VI, X $R^1=R^3=H$, $R^2=R^4=R^5=CH_3$; VII, XI $R^1=R^3=R^5=H$, $R^2=R^4=CH_3$; VIII, XII $R^2=R^4=R^5=H$, $R^1=R^3=CH_3$

Patrice Lumumba International-Friendship University, Moscow 117923. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 814-818, June, 1977. Original article submitted July 27, 1976.