## ANTHRACENE DERIVATIVES OF BENZO[f]QUINOLINE. SYNTHESIS,

## SPECTRA, AND LUMINESCENCE

N. S. Koslov, G. S. Shmanai, and L. F. Gladchenko UDC 547.832<sup>1</sup>672:543.422.6

By condensation of 9-[N-(2-naphthyl) formimidoyl]anthracene with methyl ketones under conditions of acid catalysis, 1-R-3-(9-anthryl) benzo[f]quinolines have been obtained. The byproducts of the reaction have been identified: 1-R-3-(9-anthyl)-2- propen-1-ones and N-[1-(p-aminophenyl)-3-(9-anthryl)-2- propen-1-ylidene]-2-naphthylamines. The spectral and luminenscence properties of these compounds have been examined critically.

The benzo[f]quinoline series include substances with very definite luminescing and lasing properties [1-3]. It has been of interest to obtain new compounds in this series, containing an anthracene fragment with an extended conjugation system.

A convenient method for obtaining heterocycle-substituted benzo[f]quinolines has been found recently in the reaction of condensation of azomethines — derivatives of 2-napthylamine — with CH-acid compounds. This is a multistage process in which the product of nucleophilic addition — the aminoketone A — is stabilized as a result of intramolecular dehydrocyclization, forming the benzoquinoline ring [4].

Continuing our study of this reaction in the example of 9-[N-(2-naphthyl)formimidoyl]anthracene (I), we have established that its interaction with methyl ketones of the aromatic and heterocyclic series (IIb-i) will proceed only under comparatively severe conditions; this is explained by the significant steric parameters and the electron-donor properties of the anthracene ring, lowering the reactivity of the azomethine. The optimal conditions for condensation are 2-h refluxing of the reactants with butanol in the presence of an acid catalyst and an oxidizing agent. With acetone (IIa), the reaction proceeds even at room temperature. 1-R-3-(9-anthryl)benzo[f]quinolines (IIIa-i) (Table 1) were obtained through the general scheme shown below:



II--V a  $R=CH_3$ , b  $R=C_6H_5$ , c  $R=p-CH_3C_6H_4$ , d  $R=p-FC_6H_4$ , e  $R=p-BrC_6H_4$ , f  $R=p-NO_2C_6H_4$ , g  $R=p-NH_2C_6H_4$ , h R=3-pyridyl, i R=2-quindyl.

Institute of Physical Organic Chemistry, Academy of Sciences of the Belorussian SSR, Minsk 220603. Belorussian Polytechnic Institute, Minsk. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1536-1541, November, 1985. Original article submitted December 26, 1984.

	mp,°C*	Mass spectrum		Found, %				Calc., %			
Com- pound		M⁺	intensity of [M-R] <sup>+</sup> peak, m/z 354, %	с	н	N (Br)	Empirical formula	с	н	N (Br)	Yield (%)
IIIa IIIb IIIc IIId IIIe	248-249 244-245 270-271 242-243 245-246	369 431 445 449 510	48 60 20 55 100	90,9 91,8 91,6 77,7	5,3 5,2 5,1 4,1	3,8 3,0 3,2 3,0 2,8	$\begin{array}{c} C_{29}H_{19}N\\ C_{33}H_{21}N\\ C_{34}H_{23}N\\ C_{34}H_{20}FN\\ C_{33}H_{20}FN\\ C_{33}H_{20}BrN \end{array}$	91,0 91,8 91,7 	5,2 4,9 5,2 3,9	3,8 3,2 3,1 3,1 2,7	53 50 28 14 39
IIIf IIIg IIIh IIIi	$\begin{array}{r} 283-285\\ 285-286\\ 235-236\\ 278-279\end{array}$	476 446 432 482	50 25 46 49	83,0 89,0 88,6 89,4	4,4 5,1 4,6 4,7	(15,8) 5,8 6,3 6,6 5,8	$\begin{array}{c} C_{33}H_{20}N_2O_2\\ C_{33}H_{22}N_2\\ C_{32}H_{20}N_2\\ C_{36}H_{22}N_2 \end{array}$	83,2 88,8 88,9 89,6	4,2 4,9 4,6 4,6	(15,7) 5,9 6,3 6,5 5,8	5 12 29 52

TABLE 1. Characteristics of 1-R-3-(9-anthyl)[f]quinolines IIIa-i

\*Compound IIIa was crystallized from 1:1 ethanol/toluene mixture; IIIb, c, e from toluene; IIId, f-i from dioxane.

The structure of the new products was confirmed by spectral data and elemental analysis. The benzoquinoline and anthracene rings, as structures with an aromatic character, are manifested in the IR spectra by absorption bands in the  $3070-3020 \text{ cm}^{-1}$  region from stretching vibrations of the C-H bonds of the aromatic rings, and in-plane vibrations of the skeleton in the  $1620-1500 \text{ cm}^{-1}$  region. They also give strong bands at  $900-690 \text{ cm}^{-1}$  corresponding to out-of-plane C-H vibrations in aromatic compounds. In the spectra of the nitrophenyl and aminophenyl derivatives IIIf, g, the bands of these respective functional groups are present.

In the mass spectra of the 3-(9-anthryl) derivatives of benzo[f] quinoline IIIa-i, the molecular ion peak is the most intense; there is also a rather intense peak of the 354 ion,\* indicating elimination of the substituent R (Table 1). The exception is compound IIIe, in the spectrum of which the intensity of the molecular ion peak is only 30%. There are no peaks in the spectra that would indicate fragmentation of the anthracene ring, and this is evidence of the coplanarity of this polynuclear system. Apparently, the decomposition of 1-R-3-(9-anthyl)benzo[f] quinolines when subjected to electron impact proceeds in the same general manner as the decomposition of 1-R-3-(4-quinoyl) derivatives of this series [5], in accordance with the same scheme



The UV spectra of the benzo[f]quinolines IIIa-i are characterized by an intense absorption band at 256 nm and a long-wave band in the 351-388 nm region with a distinct vibrational structure; an inflection is observed in the 270-290 nm region (Table 2, Fig. 1). The vibrational structure of the long-wave band is determined by the progression of frequencies  $1300-1400 \text{ cm}^{-1}$ , pertaining to fully symmetric vibration of the skeleton. Comparing the absorption spectra of the 1-R-3-(9-anthryl)benzo[f]quinolines with the spectra of the unsubstituted benzoquinoline and its 3-aryl derivatives [2], we should note the significant contribution of such a strong chromophore as the anthracene ring to the capability of the molecule for light absorption: In the UV spectra of the anthracene derivatives of benzoquinoline, we observe considerably higher absorption intensities and a bathochromic shift of the long-wave band (Fig. 1). The character of the substituent R has practically no influence on the spec-

\*Here and subsequently, the peaks are identified by the corresponding value of m/z.

Comp.	Absorption (in dioxane), $\lambda_{max}$ , nm	Luminescence, $\lambda_{\max}$ , nm (and $\gamma$ , %)				
	(and log $\varepsilon$ )	in benzene	in dioxane	in DMSO		
IIIa	256 (5,31), 351 (4,07), 366 (4,20), 387 (4,16)	450 (52)	450 (51)	450 (50)		
Шъ	253 (5,12), 351 (3,87), 369 (4,05), 387 (4,03)	454 (40)	454 (38)	454 (31)		
III c	256(5,20), 351(4,08), 369(4,21), 388(4,10)	454 (42)	454 (37)	460 (35)		
III d	256 (4,15) (4,00), 351 (4,00), 368 (4,18), 387 (4,16)	454 (42)	454 (39)	460 (33)		
III.e	256 (4,10) 256 (5,44), 351 (4,27), 368 (4,41), 388 (4,40)	454 (37)	454 (32)	475 (22)		
III f	256(5,25), 351(4,08), 370(4,17), 388(4,15)	Doe	s not lumin	esce		
III g	256(4,16), 351(4,27), 368(4,33), 388(4,29)	452 (45)	452 (46)	weak lumi-		
III h	256(5,22), 352(4,09), 369(4,26), 387(4,25)	455 (41)	454 (34)	475 (18)		
IIIi	256 (5,14), 351 (4,08), 369 (4,20), 388 (4,17)	470 (10)	470 (8)	505 (4)		

TABLE 2. Spectral and Luminescence Characteristics of 1-R-3-(9-Anthry1)benzo[f]quinolines IIIa-i



Fig. 1. UV spectra: 1) benzo[f]quinoline [2]; 2) 1,3-diphenylbenzo[f]quinoline [2]; 3) 1phenyl-3-(9-anthryl)benzo[f]quinoline (IIIb).

tral position of the absorption bands of the compounds IIIa-i; the various substituents give only slight changes in the absorption intensity.

All of the benzo[f]quinolines III that were investigated, with the exception of the nitro derivative IIIf, luminesce intensely in benzene or dioxane, somewhat more weakly in DMSO. The luminescence spectrum consists of a broad, unstructured band (half-width 70-80 nm) lying in the visible region of the spectrum. The substituent R in compounds IIIa-h does not influence the spectral position of the fluorescence band in nonpolar solvents; only when the quinolyl radical is introduced (compound IIIi) is the spectrum shifted bathochromically by 15-20 nm. The position of the maximum fluorescence of the anthracene derivatives of benzo[f]quinoline is also practically independent of the polarity of the solvent; however, in the spectra of compounds IIIe, h, i, in which the structure of the substituent R includes bromine or nitrogen with nonbonding electrons, we find that when the change is made to DMSO ( $\mu = 3.9$  D), there is a 20-35 nm bathochromic shift of the fluorescence band. Apparently, the dipole moment of these compounds changes slightly upon excitation, and this leads to a change in relaxation effects of orientational interaction in the system consisting of the fluorescing molecule and a polar solvent.

The considerable magnitudes of the absolute quantum yields of fluorescence  $(\gamma)$  of the benzo[f]quinolines III in benzene and dioxane provide support for the view that the synthesized compounds are coplanar. The fluorescence efficiency for these solutions is very little dependent on the character of the substituent R; only in the case of the 1-(2-quinoly1)

derivative IIIi do we observe a significant weakening of the fluorescence (Table 2). The compound fluorescing the most intensely is the 1-methyl-3-(9-anthryl)benzo[f]quinoline IIIa. The introduction of the bulky phenyl or pyridine ring (compounds IIIb-h) reduces the quantum yield of fluorescence slightly, as was also observed in a series of 3-arylbenzoquinolines[2].

An increase in the dipole moment of the solvent leads to a certain decrease in the fluorescence intensity for the compounds we have examined. The most probable reason for this effect is a strengthening of intermolecular interaction of the polar solvent with the hetero atom of the benzoquinoline ring (in compounds IIIh, i, also with the nitrogen of the pyridine or quinoline ring), leading to disruption of the coplanarity of the molecule. The quenching of fluorescence by the amino derivative IIIg in DMSO is due to the formation of a strong hydrogen bond between the solvent and the terminal amino group, of the type N-H...O =  $S(CH_3)_2$ , as has been noted previously for hydroxystyryl derivatives of benzo[f]quinoline [3].

When the azomethine I interacts with the ketones IIf, g, the main products are 1-R-3-(9-anthryl)-2-propen-1-ones (IVf, g). The desired benzoquinolines IIIf, g are formed only in small yields, even in the presence of a "tamed acid" - 2-naphthylamine hydrochloride. In the IR spectra of the propenones there is a band of stretching vibrations of the conjugated carbonyl group. In the mass spectra of compounds IVf, g, in addition to the molecular ion peak, there is a characteristic peak of the  $\beta$ -(9-anthryl)vinylene cation; in the spectrum of the amino derivative IVg, peaks are also noted at 92, 120, and 294, corresponding to the ions [NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>]<sup>\*+</sup>, [NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CO]<sup>+</sup>, and [M-H-CO]<sup>+</sup> (see experimental section). This indicates rupture of C-C bonds alongside the carbonyl group.

The formation of the propenones IV under the conditions of reaction is possible as a result of a competing process of hydramine cleavage of the aminoketone A, and also as a result of the reaction of aldol condensation of the ketones II with the aldehyde formed by hydrolysis of the azomethine in the acidic medium. The susceptibility of  $\beta$ -anilinopropiophenones to hydramine cleavage is well known [6, 7].

It was suggested in [8] that  $\beta$ -aminoketones with a 2-naphthylamine fragment are also subject to hydrolysis. In the present work, this has been demonstrated indirectly. We have established that in this case, the second path of formation of the propenones IV can be excluded from consideration, since we were not able to obtain them in acidic medium from 9anthranyl aldehyde and substituted acetophenones.

Upon condensation of the azomethine I with aminoacetophenone IIg, we recovered, in addition to the benzoquinoline IIIg and the propenone IVg, N-[1-(p-aminopheny1)-3-(9-anthry1)-2propen-1-ylidene]-2-naphthylamine (Vg), the structure of which was established on the basis of chemical conversions and spectral data. Upon heating the compound Vg in an acidic medium, hydrolysis of the C=N bond takes place, forming the propenone IVg and 2-naphthylamine. The structure proposed for the imine Vg is confirmed by the presence of peaks in the mass spectrum indicating fragmentation of the  $\beta$ -(9-anthry1)vinylene grouping.

## EXPERIMENTAL

The IR spectra were recorded in a UR-20 spectrophotometer in KBr tablets; the UV spectra were recorded in a Specord UV-Vis instrument, in dioxane. The mass spectra were obtained in a Varian MAT-311 instrument with direct introduction of the substance into the ion source, with an ionizing voltage of 70 eV and an admission temperature 15-20° below the melting point of the sample. The fluorescence spectra were measured in a Fica-55 absolute spectrofluorimeter. The fluorescence was excited at a wavelength of 378 nm, which falls into the long-wave absorption band. The absolute quantum yields of fluorescence were calculated by a relative method. As the standard we used a solution of 3-amino-N-methylphthalimide in ethanol, for which the absolute quantum yield of fluorescence is 60%. The relative error in measuring  $\gamma$  was 3-5%. The purity of the substances was monitored by means of TLC in an unanchored bed of Al<sub>2</sub>O<sub>3</sub> (standard activity II) in benzene, developed in iodine vapor.

The 9-[N-(2-naphthyl)formimidoyl]anthracene I was obtained in accordance with [9]; the 2-acetylquinoline IIi was obtained by a procedure described for the 4-isomer [10]. The yields and characteristics of the benzoquinolines IIIa-i are given in Tables 1 and 2.

<u>1-Phenyl-3-(9-anthryl)benzo[f]quinoline (IIIb).</u> A mixture of 1.65 g (5 mmoles) of the azomethine I, 0.8 g (6 mmoles) of acetophenone IIb, 35 ml of n-butanol, 5 drops of concentrated HCl, and 5 drops of nitrobenzene was refluxed for 2 h. The reaction mixture was evaporated under vacuum to 1/3 its original volume, 10 ml of ethanol was added, and the solution

was neutralized with NH4OH. The precipitate of IIIb was separated off, washed with ethanol and water, and dried, after which it was crystallized from toluene.

Compounds IIIc, d, e, h, i were obtained analogously; the benzoquinoline IIIa was obtained at room temperature (20 days).

<u>1-(p-Nitrophenyl)-3-(9-anthryl)benzo[f]quinolines (IIIf) and 1-(p-nitrophenyl)-3-(9-an-thryl)-2-propen-1-one (IVe).</u> A mixture of 1.65 g (5 mmoles) of the azomethine I, 1.0 g (6 mmoles) of the ketone IIf, 1.1 g (6 mmoles) of 2-naphthylamine hydrochloride, 35 ml of n-butanol, and 5 drops of nitrobenzene was refluxed for 2 h. In the course of the reaction, the propenone IVf crystallized out; after cooling, it was filtered off. The benzoquinoline IIIf was recovered as described above for compound IIIb; the propenone IVf was 1.3 g (74%); mp 154-155° (acetone). IR spectrum (cm<sup>-1</sup>): 1658 (C=N), 1528 and 1345 cm<sup>-1</sup> (NO<sub>2</sub>). UV spectrum,  $\gamma_{max}$  (in nm) (and log  $\varepsilon$ ): 253 (5.27), 270 (4.50), 360 (3.84), 380 (3.84). Mass spectrum, m/z (relative intensity, %): 353 (38), 203 (100). Found: C 78.3; H 4.4; N 4.1%. C<sub>23</sub>H<sub>13</sub>NO<sub>3</sub>. Calculated: C 78.2; H 4.3; N 4.0%.

1-(p-Aminopheny1)-3-(9-anthry1)benzo[f]quinoline (IIIg), 1-(p-aminopheny1)-3-(9-anthry1)-2-propen-1-one (IVg), and N-[1-(p-aminopheny1)-3-(9-anthry1)-propen-1-ylidene]-2-naphthylamine (Vg) were obtained by analogy with compounds IIIf and IVf, from 1.65 g (5 nmoles) of the azomethine I and 0.75 g (6 mmoles) of the ketone IIg. Upon concentration of the reaction mass, a mixture of the propenone IVg and the imine  $V_g$  precipitated out. The precipitate was neutralized with NH4OH and washed with water and hot acetone (10 ml), after which the propenone IVg was washed out; yield 0.48 g (30%), mp 189-190° (ethanol). IR spectrum (cm<sup>-1</sup>): 1650 (C=0), 3480, 3340, and 3230 cm<sup>-1</sup> (N-H). UV spectrum  $\lambda_{max}$  (in nm) (and log  $\epsilon$ ): 251 (5.16), 350 (4.26), 365 (4.26), 384 (4.19). Mass spectrum, m/z (relative intensity, %): 323 (50), 294 (7), 202 (28), 178 (10), 120 (100), 92 (27). Found: C 85.6; H 5.3%. C23H17NO. Calculated: C 85.5; H 5.3%. The imine Vg was crystallized from benzene; yield 0.27 g (12%), mp 215-216°. IR spectrum (cm<sup>-1</sup>): 3450, 3370, 3220 cm<sup>-1</sup> (N-H). UV spectrum,  $\lambda_{max}$  (in nm) (and log  $\epsilon$ ): 252 (5.07), 365 (4.18), 384 (4.18). Mass spectrum, m/z (relative intensity, %): 448 (100), 354 (10), 271 (58), 270 (48), 245 (20), 224 (10), 202 (12), 178 (30), 143 (23), 127 (23). Found: C 88.3; H 5.5; N 6.3%. C33H24N2. Calculated: C 88.4; H 5.4; N 6.3%. From the neutralized mother liquor, the benzoquinoline IIIg was recovered, after which it was washed with hot acetone and crystallized from dioxane.

Hydrolysis of N-[1-(p-aminophenyl)-3-(9-anthryl)-2-propen-1-ylidene]-2-naphthylamine (Vg). A mixture of 1.1 g (2.5 mmoles) of the imine Vg, 15 ml of butanol, 3 drops of concentrated HC1, and 3 drops of nitrobenzene was refluxed for 2 h. After boiling down the reaction mixture to 1/3 of its original volume, 0.7 g (30%) of the propenone IVg was recovered, and from the mother liquor 0.4 g (60%) of 2-naphthylamine.

## LITERATURE CITED

- 1. R. H. Wiley, C. H. Jarboe, and F. N. Hayes, J. Org. Chem., 23, 268 (1958).
- 2. N. S. Kozlov, L. F. Gladchenko, V. A. Serzhanina, G. V. Vorob'eva, O. D. Zhikhareva,
- G. S. Shmanai, and R. D. Sauts, Khim. Geterotsikl. Soedin., No. 9, 1237 (1977).
- N. S. Kozlov, L. F. Gladchenko, V. A. Serzhanina, G. S. Shmanai, I. P. Stremok, G. P. Korotyshova, and R. D. Sauts, Khim. Geterotsikl. Soedin., No. 4, 511 (1978).
- 4. N. S. Kozlov, G. V. Vorob'eva, and G. S. Bychkova, Izv. Akad. Nauk BSSR, Ser. Khim.
- 4. N. S. KOZIOV, G. V. VOROD eva, and G. S. Bychkova, 12V. Akad. Nauk BSSK, Ser. Kilm. Nauk, No. 5, 80 (1969).
- 5. N. S. Kozlov, G. S. Shmanai, V. P. Suboch, and V. I. Vil'chinskaya, Khim. Geterotsikl. Soedin., No. 4, 520 (1979).
- 6. N. S. Kozlov and I. A. Shur, Zh. Obshch. Khim., 29, 2706 (1959).
- 7. A. T. Babayan and N. P. Gambaryan, Izv. Akad. Nauk Arm. SSR, Fiz.-Mat. Estestv. Tekh. Nauki, 6, 99 (1953).
- 8. N. S. Kozlov, G. V. Vorob'eva, and I. P. Mikhailova, Khim. Geterotsikl. Soedin., No. 9, 1243 (1979).
- 9. W. W. John, J. W. W. Scott, and W. H. Jura, Can. J. Chem., 45, 2375 (1967).
- 10. K. N. Campbell and J. F. Kerwin, J. Am. Chem. Soc., <u>68</u>, 1837 (1946).