

# HEMICYANINES FROM 3-ARYLBENZO[f]QUINOLINIUM SALTS AND THEIR SPECTRAL-LUMINESCENCE PROPERTIES

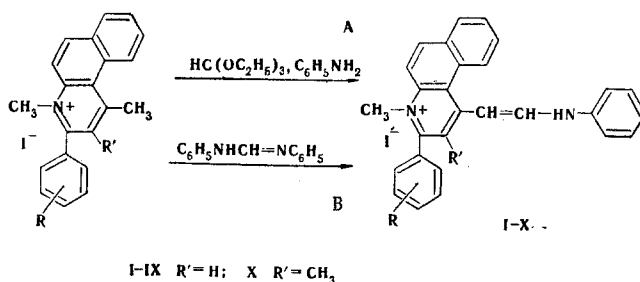
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1-( $\beta$ -Anilinoethyl)-3-arylbenzo[f]quinolinium methiodides were synthesized by the condensation of 1,4-dimethyl-3-arylbenzo[f]quinolinium salts with ethyl orthoformate and aniline or by fusion with N,N-diphenylformamidine. The IR spectra, the absorption spectra in the visible region, and the fluorescence of the dyes in the crystalline state were examined. The introduction of substituents in the 3-phenyl ring of benzo[f]quinoline gives rise to a bathochromic shift of the fluorescence band.

Many derivatives of heterocyclic compounds have found application as organic luminophores. Thus, aryl- and arylolefin derivatives of benzimidazoles, benzoxazoles, and naphthalimide are used as activating additives in liquid and plastic scintillators, as dyes for plastics, and as fluorescing pigments [1].

Continuing our study of the spectral-luminescence characteristics of benzo[f]quinoline derivatives that was begun in [2], we synthesized a number of hemicyanines, viz.,  $\beta$ -anilinoethyl derivatives of 3-arylbenzo[f]quinolinium salts (I-X). Hemicyanines are intermediates in the synthesis of cyanine dyes with unsymmetrical structures [3] and also find application as sensitizers and desensitizers of silver halide emulsions [4]. The synthesis of hemicyanines I-X was realized by two methods, viz., by condensation of quaternary 1,4-dimethyl-3-arylbenzo[f]quinolinium salts with ethyl orthoformate and aniline (A) and with N,N-diphenylformamidine (B).



The reaction in both cases proceeds with the formation of  $\beta$ -anilinoethyl derivatives of 3-arylbenzo[f]quinolinium salts. The dyes obtained by method B are purer and are obtained in higher yields, and the reaction time in the case of heating in vacuo is shortened. This condensation does not occur by the method described in [5] in the case of benzo[f]quinolinium salts in anhydrous acetic acid.

The structures of the hemicyanines are confirmed by data from the IR and UV spectra. The presence of an ethylene double bond is characterized by a set of absorption bands of medium and strong intensity at 3000-3040, 930-970, and 1280-1310  $\text{cm}^{-1}$  (C-H stretching and deformation vibrations). The absorption band at 930-970  $\text{cm}^{-1}$  constitutes evidence for a trans configuration at the ethylene double bond [6]. The C=C stretching vibrations of both an ethylene bond and an aromatic system are observed at 1600-1640  $\text{cm}^{-1}$ . The broad band of medium intensity at 3440  $\text{cm}^{-1}$  is related to the stretching vibrations of the NH group. It is sometimes overlapped by the band of C-H absorption.

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TABLE 1. 1-( $\beta$ -Anilino vinyl)-3-(R-phenyl)benzo[f]quinolinium Methiodides

Compound	R	mp, °C	Adsorption $\lambda_{\max}$ , nm (log $\epsilon$ )	Fluorescence, $\lambda_{\max}$ , nm	Found, %			Empirical formula	Calc., %			Yield, %
					C	H	Hal		C	H	Hal	
I	H	222—223	511 (4.69)	600	65.0	4.8	25.1	C <sub>28</sub> H <sub>23</sub> IN <sub>2</sub>	65.4	4.5	24.7	47
II	4-CH <sub>3</sub> O	210—212	508 (4.72)	648	63.8	4.6	23.3	C <sub>29</sub> H <sub>25</sub> IN <sub>2</sub> O	64.0	4.6	23.3	61
III	3,4-(OCH <sub>2</sub> O)	224	509 (4.73)	655	62.4	4.3	22.8	C <sub>29</sub> H <sub>23</sub> IN <sub>2</sub> O <sub>3</sub>	62.4	4.1	22.8	36
IV	3,4-(CH <sub>3</sub> O) <sub>2</sub>	239—240	508 (4.67)	665	62.7	4.8	21.8	C <sub>30</sub> H <sub>27</sub> IN <sub>2</sub> O <sub>2</sub>	62.7	4.7	22.1	40
V	2,4-(CH <sub>3</sub> O) <sub>2</sub>	242—243	505 (4.67)	651	62.2	4.5	22.2	C <sub>30</sub> H <sub>27</sub> IN <sub>2</sub> O <sub>2</sub>	62.7	4.7	22.1	42
VI	2-HO—3-CH <sub>3</sub> O	200—201	505 (4.76)	619	61.8	4.8	22.2	C <sub>29</sub> H <sub>25</sub> IN <sub>2</sub> O <sub>3</sub>	62.1	4.5	22.7	57
VII	4-F	238	507 (4.66)	614, 659	61.0	4.1	22.9	C <sub>28</sub> H <sub>22</sub> FIN <sub>2</sub> *	61.2	4.0	29.6	41
VIII	4-Cl	241—242	507 (4.70)	650	61.0	4.1	22.9	C <sub>28</sub> H <sub>22</sub> ClIN <sub>2</sub>	61.2	4.0	29.6	74
IX	4-Br	228	509 (4.66)	683	56.6	4.0	34.9	C <sub>28</sub> H <sub>22</sub> BrIN <sub>2</sub>	56.7	3.7	34.9	81
X	4-NO <sub>2</sub>	188—190	519 (4.46)	—	60.9	4.3	22.1	C <sub>29</sub> H <sub>24</sub> IN <sub>3</sub> O <sub>2</sub>	60.7	4.2	22.2	31

\* Found: N 5.4%. Calculated: N 5.3%.

The absorption bands that are characteristic for the starting quaternary salts (370–390 nm) are retained in the UV spectra of the hemicyanines, but an intense long-wave band at 505–519 nm, which is associated with a  $\pi$ – $\pi^*$  electron transition, also appears. This band is shifted hypsochromically as compared with the analogous band of the p-dimethylaminostyryl derivatives of 3-arylbenzo[f]quinolinium salts obtained in [7, 8], which is associated with shortening of the conjugation chain.

The investigated dyes fluoresce both in solutions and in the crystalline state. However, they fluoresce weakly in solutions. This is explained by the fact that the probability of rotation of the anilino vinyl group relative to the benzoquinoline fragment of the molecule decreases in the crystalline state. In solutions this rotation leads to the additional loss of excitation energy, as a consequence of which the fluorescence efficiency decreases [9]. The fluorescence maximum of the crystals is found at 600–683 nm. Substituents in the 3-phenyl ring do not have a significant effect on the position of the maximum of the long-wave absorption band. However, they have an appreciable effect on the position of the fluorescence band (Table 1). Thus, the introduction of a methoxy group leads to a considerable bathochromic shift (II), and the effect becomes more intense when an OCH<sub>2</sub>O group and a second CH<sub>3</sub>O group are introduced (III–V). The introduction of a halogen, particularly bromine, also leads to a bathochromic effect. The increase in the intensity of the fluorescence for compounds that contain a methoxy group as a substituent, which we noted in [2], should be noted.

## EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The UV absorption spectra of solutions of the dyes in ethanol ( $c$   $10^{-4}$  M) were recorded with a Specord UV-vis spectrophotometer. The fluorescence spectra were measured with a Fika-55 absolute spectrofluorimeter; excitation was realized in the region of the long-wave absorption band (the excitation wavelength of the crystals was 505 nm).

1-( $\beta$ -Anilino vinyl)-3-(p-chlorophenyl)benzo[f]quinoline Methiodide (VIII). A) A mixture of 0.45 g (1 mmole) of 1-methyl-3-(p-chlorophenyl)benzo[f]quinoline methiodide, 0.3 ml (2 mmole) of ethyl orthoformate, and 0.5 ml (5 mmole) of aniline was refluxed at 120°C for 1.5 h, and the dark-red melt was treated with heating with acetone until it was converted to a powder. The powder was removed by filtration, washed with ether, and crystallized from a mixture of alcohol with nitromethane to give a product with mp 232°C in 31% yield.

B) A mixture of 1 mmole of the quaternary salt and 2 mmole of N,N-diphenylformamidine was triturated in a mortar and heated at 120°C for 1.5 h. Workup gave a product with mp 241–242°C in 74% yield.

The remaining dyes (Table 1) were similarly obtained by method B. Dye IX was heated for 5 h; the yield was 42%. The yield was increased to 81% by heating at 160°C for 10 min or at 140°C for 50 min.

1-( $\beta$ -Anilino vinyl)-2-methyl-3-(p-nitrophenyl)benzo[f]quinoline Methiodide (X). A mixture of 0.45 g (1 mmole) of 1,2-dimethyl-3-(p-nitrophenyl)benzo[f]quinoline methiodide [10] and 0.4 g (2 mmole) of N,N-diphenylformamidine was heated in vacuo at 160°C for 10 min and at 130–140°C for 40 min. The melt was treated with acetone and washed with ether.

## LITERATURE CITED

1. B. M. Krasovitskii and B. M. Bolotin, Organic Luminophores [in Russian], Khimiya, Leningrad (1976).
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).
3. J. Ogata, Chem. Zentralblatt, II, 711 (1932).
4. A. Van Dormael and A. De Cat, Bull. Soc. Chim. Belg., 58, 487 (1949).
5. G. N. Dorofeenko, V. V. Mezheritskii, and A. L. Vasserman, Khim. Geterotsikl. Soedin., No. 10, 1338 (1974).
6. L. Bellamy, Infrared Spectra of Complex Molecules, Methuen, London (1957).
7. N. S. Kozlov and O. D. Zhikhareva, Dokl. Akad. Nauk Belorussk. SSR, 16, 629 (1972).
8. N. S. Kozlov, O. D. Zhikhareva, and I. P. Stremok, Dokl. Akad. Nauk Belorussk. SSR, 18, 46 (1974).
9. P. Prinsheim and M. Vogel, Luminescence of Liquids and Solids [Russian translation], Moscow (1948).
10. N. S. Kozlov, O. D. Zhikhareva, and I. P. Stremok, Dokl. Akad. Nauk Belorussk. SSR, 21, 425 (1977).

## SYNTHESIS OF DERIVATIVES OF 7-iodo-4-AMINOQUINOLINES

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7-Iodo- and 7,8-diiodo-4-(3-dimethylaminopropylamino)quinolines and 7-iodo-4-(3)dipropylaminopropylamino)- and 7-iodo-4-(3-diallylamino)propylamino)quinoline were obtained by the reaction of 7-iodo- and 7,8-diiodo-4-chloroquinolines with the corresponding diamines. The catalytic hydrogenation of 7-iodo-4-(3-diallylamino)propylamino)quinoline at normal pressure leads to 7-iodo-4-(3-dipropylaminopropylamino)quinoline.

The biological activity of substituted 4-aminoquinolines has been the subject of intensive studies (for example, see [1-6]). A study of the distribution of these compounds in individual organs and tissues of organisms made it necessary to synthesize radioisotope-labeled aminoquinolines. For example, 7-<sup>131</sup>I-4-(3-dimethylaminopropylamino)quinoline and its analogs are localized in malignant tumors [1-4].

The aim of the present research was to synthesize 7-iodo-4-(3-dimethylaminopropylamino)quinoline (I) and the analogous II-VI, in the molecules of which iodine or hydrogen radioisotopes can be easily introduced.

4-Aminoquinolines I-VI were obtained in analytically pure form by heating mixtures of 4-chloroquinolines VII or VIII and the corresponding diamines (Table 1). A similar previously known method for the synthesis of quinoline I [1] was poorly reproduced and did not make it possible to obtain significant amounts of a preparation with a high degree of purity. We established that quinolines I-VI can be obtained only when thoroughly purified starting 4-chloroquinolines VII and VIII and diamines were used.

4-Chloro-7,8-diiodoquinoline (VIII) was obtained from 4-chloro-7-iodoquinoline (VII). The nitration of quinoline VII with excess fuming nitric acid at 100°C gives 4-chloro-7-iodo-8-nitroquinoline (IX), which is reduced by stannous chloride to 4-chloro-7-iodo-8-aminoquinoline (X) with admixed 4-chloro-8-aminoquinoline. Aminoquinoline X was converted to diiodoquinoline VIII via the Sandmeyer reaction.

The results of elementary analysis and data from thin-layer chromatography (TLC) and the PMR and UV spectra (Tables 1 and 2) confirm the individuality and structures of quinolines I-X. The expected quinoline II is formed in 53% yield in the catalytic hydrogenation of quinoline IV at normal pressure in the presence of 10% platinum on silica gel. Virtually no hydrogenolysis of the C-N bond occurs under these conditions.