1-Phenyl-2-acetyl-5-methyltetrahydropyridazino[4,5-b]indole (VII). A 2.63 g (0.01 mole) sample of base VIa was refluxed in 50 ml of acetic anhydride for 20 min, after which it was cooled, and the precipitated crystals of VII were purified by crystallization from ethanol to give 2.38 g (78%) of a product with mp 218°. Found: N 13.7%. $C_{20}H_{17}N_3O_2$. Calculated: N 13.8%.

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1-ETHYL- AND 1,2-DIMETHYL-3-(p-METHOXYPHENYL)BENZO[f]QUINOLINES AND THEIR TRANSFORMATIONS

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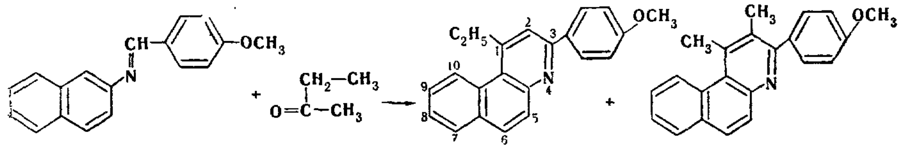
UDC 668.8.547.832.5:543.422.25.4.5.6:542.953

Condensation of p-methoxybenzylidene-2-naphthylamine with methyl ethyl ketone leads to a mixture of 1-ethyl- and 1,2-dimethyl-3-(p-methoxyphenyl)benzo[f]quinolines, for which protic and quaternary salts were obtained. Cyanine dyes were synthesized from 1,2-dimethyl-3-(p-methoxyphenyl)benzo[f]quinoline methiodide.

The condensation of p-methoxybenzylidene-2-naphthylamine with methyl ethyl ketone in acidic media proceeds simultaneously in two directions — at the methyl and methylene groups to give I and II.



I II

The PMR spectra demonstrated that the products contain both isomers in approximately equal ratios. The separation of I and II was based on the different solubilities of their hydrochlorides in ethanol. In addition to I and II, we also isolated the dihydro derivative of benzo[f]quinoline, the IR spectrum of which contains the characteristic band of the NH group at 3450 (in CCl_4) and 3410 cm^{-1} (KBr). This band is absent in the IR spectra of I and II.

Substituents in the benzo[f]quinoline ring and steric factors to a considerable degree determine the character of the absorption in the UV spectra of I and II, which contain absorption bands characteristic for benzo[f]quinolines with respect to the form, number, and position of the maxima [1-3]. A hypsochromic shift of the p and α bands as compared with

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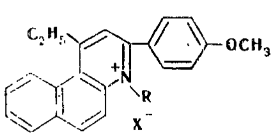
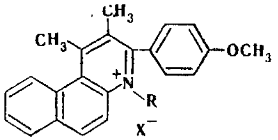
TABLE 1. Characteristics of Benzo[f]quinolines and Their Salts





Compound	R	X⁻	mp, °C	Empirical formula	Found, %			Calc., %			UV spectra, λ_{max}, nm (log ε)	Yield, %
					C	H		C	H			
I	—	—	124—126	$C_{22}H_{19}NO$	84,5	6,3	N 4,4	84,3	6,1	N 4,5	217, 227, 268, 285, 347, 364 (4,33; 4,31; 4,46; 4,57; 3,88; 3,89)	16
II	—	—	187—188	$C_{22}H_{19}NO$	84,7	6,3	N 4,4	84,3	6,1	N 4,5	219, 258, 273, 328, 341, 356 (4,39; 4,54; 4,47; 3,50; 3,70; 3,74)	12
Ia	CH_3	I	236—238	$C_{23}H_{22}INO$	60,8	4,9	I 27,9	60,7	4,8	I 27,9	218, 230, 284, 348, 365, 386 (4,66; 4,56; 4,50; 3,97; 4,06; 3,87)	55
IIa	CH_3	I	208	$C_{23}H_{22}INO$	60,9	4,9	I 27,8	60,7	4,8	I 27,9	221, 241, 281, 318, 365, 379 (4,81; 4,64; 4,66; 3,98; 4,19; 4,28)	92
Ib	H	$C_6H_2N_3O_7$	189—190	$C_{22}H_{19}NO \cdot C_6H_3N_3O_7$	62.2	4,3	N 10,2	62,0	4,0	N 10,3	217, 231, 284, 347, 364, 391 (4,49; 4,46; 4,56; 4,25; 4,28; 3,99)	92
IIb	H	$C_6H_2N_3O_7$	211—212	$C_{22}H_{19}NO \cdot C_6H_3N_3O_7$	62,1	4,1	N 10,1	62,0	4,0	N 10,3	219, 247, 276, 343, 358, 391 (4,62; 4,63; 4,53; 4,25; 4,35; 3,90)	100
Ic	H	ClO_4	275	$C_{22}H_{19}NO \cdot HClO_4$	63,7	4,9	Cl 8,7	63,8	4,8	Cl 8,6	237, 282, 313, 389 (4,56; 4,38; 4,41; 4,48)	83
IIc	H	ClO_4	261—262	$C_{22}H_{19}NO \cdot HClO_4$	63,9	5,2	Cl 8,3	63,8	4,8	Cl 8,6	220, 256, 278, 342, 359, 377 (4,50; 4,57; 4,56; 3,84; 3,94; 3,72)	75
Id	CH_3	CH_3SO_4	282—283	$C_{24}H_{25}NO_5S$	65.4	5,7	S 7,1	65,6	5,7	S 7,3	218, 232, 284, 347, 364, 388 (4,35; 4,37; 4,60; 3,91; 3,96; 3,48)	27
IId	CH_3	CH_3SO_4	240—242	$C_{24}H_{25}NO_5S$	65,7	5,9	S 7,4	65,6	5,7	S 7,3	218, 259, 342, 357, 384 (4,36; 4,47; 3,67; 3,74; 3,15)	27
Ie	CH_3	ClO_4	284—285	$C_{23}H_{22}ClNO_5$	64.5	5,3	Cl 8,2	64,6	5,1	Cl 8,3	218, 232, 285, 347, 364, 384 (4,33; 4,33; 4,61; 3,90; 3,93; 3,27)	95
IIe	CH_3	ClO_4	264—265	$C_{23}H_{22}ClNO_5$	64,6	5,4	Cl 8,5	64,6	5,1	Cl 8,3	220, 257, 278, 343, 347, 377 (4,41; 4,50; 4,49; 3,70; 3,84; 3,63)	90

the spectrum of I is observed in the spectrum of II; this shift is due to the steric hindrance arising between the methyl group in the 2 position and the substituents in the 1 and 3 positions of the benzo[f]quinoline ring (Table 1).

The structures of I and II were also confirmed by means of their PMR spectra [4]. Signals of protons at 2.48 (t), 3.46 (q, J = 8.0 Hz, C_2H_5 group) and 7.84 ppm (s, 2-H) are observed in the PMR spectrum of I; in the spectrum of II the methyl groups in the 1 and 2 positions have chemical shifts of 2.94 and 2.44 ppm.

The UV spectra of salts I-IIa-e are basically analogous to the spectra of bases I and II, but an additional long-wave absorption maximum appears at 377-391 nm (Table 1). Intense bands at 1110-1124 cm^{-1}, related to the vibrations of the ClO_4^- anion (I and IIc,e), are observed in the IR spectra of the salts; the bands at 1540, 1515, 1492, and 1368, 1365, and 1335 cm^{-1} are associated with the vibrations of a nitro group (I and IIb), and the bands at 1378, 1350, and 1325 and to 1195 and 1180 cm^{-1} are characteristic for the SO_2 group (I and IId) [5].

1,2-Dimethyl-3-(p-methoxyphenyl)benzo[f]quinoline methiodide (IIa) under the usual conditions gives polymethine dyes — a trimethylidynecyanine (III), a hydroxystyryl (IV), and a merocyanine (V) — since it contains an active methyl group in the 1 position of the benzo[f]quinoline ring. However, the steric hindrance in the pyridine ring of the benzo[f]quinoline II created by bulky substituents leads to slowing down of the cyanine condensation (3 h) and a decrease in the intensity of the absorption of the dyes. We were unable to obtain dyes for methiodide Ia.

EXPERIMENTAL

The UV absorption spectra of ethanol solutions of the compounds (c 10^{-4} M) were recorded with a Specord UV-vis spectrophotometer. The IR spectra of KBr pellets were obtained with a UR-20 spectrometer. The PMR spectra of $CDCl_3$ solutions of the compounds containing hexamethyldisiloxane (I) and tetramethylsilane (II) as internal standards were recorded with a JNM-PS-100 spectrometer (100 MHz).

1-Ethyl-3-(p-methoxyphenyl)benzo[f]quinoline (I) and 1,2-Dimethyl-3-(p-methoxyphenyl)benzo[f]quinoline (II). A mixture of 5.4 ml (60 mmole) of methyl ethyl ketone, 4 ml of concentrated HCl, and 0.4 ml of nitrobenzene in 5 ml of ethanol was added to a solution of 5.2 g (20 mmole) of p-methoxybenzylidene-2-naphthylamine in 15 ml of ethanol, and the mixture was refluxed on a water bath for 3 h. The next day, the precipitated hydrochloride of I was removed by filtration, dissolved in ethanol, and neutralized with 10% NH_4OH. The mother ethanol solution was subjected to the same neutralization to yield II. The precipitates were washed with water, dried, and crystallized two to three times from ethanol—toluene (5:1) to give 1.02 g of colorless needles of I and 0.76 g of colorless needles of II (Table 1).

The methiodides, picrates, and perchlorates were obtained by standard methods and crystallized from ethanol and acetone. The methylsulfates were obtained by heating the bases with dimethyl sulfate in nitrobenzene at 100° for 8-10 h and workup of the resinous precipitate by treatment with toluene, ether, and acetone and crystallization from acetic acid. The methyl perchlorates were obtained from the methylsulfates by reaction with 42% $HClO_4$ in ethanol and were crystallized from ethanol—nitromethane.

Bis[2,4-dimethyl-3-(p-methoxyphenyl)benzo[f]quinol-1-yl]trimethylidynecyaninium Iodide (III). A mixture of 0.46 g (1 mmole) of methiodide IIa, 0.8 ml of ethyl orthoformate, 3 ml of pyridine, and four drops of acetic anhydride was heated at 130-140° for 3 h, after which the dye was precipitated by the addition of ether and crystallized twice from ethanol to give 0.1 g (25%) of dark-green crystals with mp 185°. UV spectrum: λ_{max} 768 nm (log ε 4.38). Found: C 71.0; H 5.1; I 16.4%. $C_{47}H_{41}IN_2O_2$. Calculated · C 71.2; H 5.2; I 16.0%.

1-[(2-Hydroxy-5,6-benzostyryl)-2-methyl-3-(p-methoxyphenyl)]benzo[f]quinoline methiodide (IV). A mixture of 0.46 g (1 mmole) of methiodide IIa, 0.2 g (1 mmole) of 1-formyl-2-hydroxynaphthalene, 5 ml of absolute ethanol, and five drops of piperidine was heated on a boiling-water bath for 3 h, and the resulting precipitate was removed by filtration, washed with water and ether, and crystallized from ethanol—acetone (1:3) to give 0.22 g (37%) of yellow-brown prisms with mp 240-241°. UV spectrum: λ_{max} 455 and 678 nm (log ε 3.84 and 3.38). Found: C 67.1; H 4.9; I 20.8%. $C_{34}H_{28}INO_2$. Calculated: C 67.0; H 4.6; I 20.8%.

[2,4-Dimethyl-3-(p-methoxyphenyl)benzo[f]dihydro-1-quinolylidene]-(5,6-benzo-2-quino]-ethane (V) [6]. A 0.07-g (0.1 mmole) sample of hydroxystyryl IV was dissolved by heating in 30 ml of ethanol, after which 10 ml of 10% aqueous KOH solution was added, and the mixture was heated on a water bath for 5 min. After 30 min, the resulting precipitate was removed by filtration, washed with water, dried, and crystallized from the ethanol—acetone (1:2) to give 0.03 g (62%) of shiny violet plates with mp 172-174°. UV spectrum: λ_{max} 668 nm (log ε 3.0); in acetone 696 (log ε 3.25); in chloroform 706 nm (log ε 4.60. Found: C 81.7; H 5.9%. $C_{34}H_{27}NO_2 \cdot H_2O$. Calculated: C 81.8; H 5.8%.

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MECHANISM OF NUCLEOPHILIC SUBSTITUTION OF HYDROGEN IN AZINES.

II.* KINETICS OF THE CONDENSATION OF N-METHYLACRIDINIUM IODIDE WITH AROMATIC AMINES

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A study of the kinetics of the reaction of N-methylacridinium iodide with arylamines shows that the reaction proceeds via a stepwise bimolecular mechanism with the formation of an intermediate.

The mechanism of reactions involving the nucleophilic substitution of hydrogen in the azine series has often been postulated as "addition—cleavage" [2-4]. However, data that show that even the well-studied nucleophilic substitution of halogen in aromatic nitro compounds cannot always be interpreted within the framework of this mechanism were recently obtained [5]. The mechanism of reactions involving nucleophilic substitution of aromatically bonded hydrogen in azines has been investigated kinetically only in one study [1] in the case of the reaction of the acridinium cation with active methyl-substituted heterocycles. This reaction evidently proceeds with the participation of the carbanion of the CH-active compound. The kinetics of the reactions of azinium cations with uncharged nucleophiles have not been investigated, although the absence of a charge on the nucleophile may superimpose peculiarities on the trend of the process.

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*See [1] for communication I.

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