AZOMETHINE AND MEROCYANINE DYES BASED ON 3-ARYLBENZO[f]QUINOLINIUM SALTS AND THEIR SPECTRAL AND ELECTROPHOTOGRAPHIC PROPERTIES

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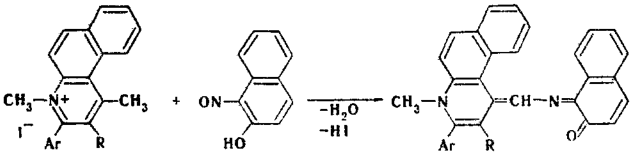
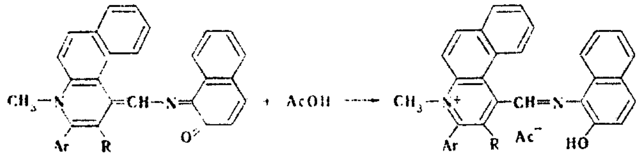
Azomethine dyes were obtained by reaction of 1-methyl- and 1,2-dimethyl-3-arylbenzo[f]quinolinium methiodides with 1-nitroso-2-naphthol. Merocyanine dyes were isolated by the action of KOH on 2-hydroxy-5,6-benzostyryl derivatives of 3-arylbenzo[f]quinolinium salts. The absorption spectra of the dyes in ethanol and chloroform are presented, and it is shown that, as compared with the spectra of the merocyanines, there is a bathochromic shift of the absorption bands in the spectra of the azomethine dyes. The azomethine and merocyanine dyes have solvatochromic properties and display photosensitivity in the UV and visible regions when they are introduced into a polymer matrix.

Azomethine dyes are formed in the reaction of quaternary heterocyclic salts containing an active methyl group with 1-nitroso-2-naphthol [1, 2]. Dyes of this type are used in color photography in multilayer films with color development as dyes for sharp images [3].



I a-g R=H; I h R=CH_3 Ia-h

1-Methyl- and 1,2-dimethyl-3-arylbenzo[f]quinolinium methiodides undergo condensation with 1-nitroso-2-naphthol to give azomethine dyes I, the characteristics of which are presented in Table 1. Alcohol solutions of azomethines I are green (λ_{max} 700-722 nm). They are decolorized when mineral acids (HCl, H_2SO_4) are added, whereas when acetic acid is added, the azomethine bases are converted to salts, and the color of the solutions changes to yellow-orange (λ_{max} 425-512 nm) (Table 2).



IIa-h

By treatment of the 2-hydroxy-5,6-benzostyryl derivatives of 3-arylbenzo[f]quinolinium salts with KOH by the method in [4] we obtained merocyanine dyes III (Table 3), which differ from azomethine dyes I only with respect to replacement of the nitrogen atom in the chain by a methylidyne group:

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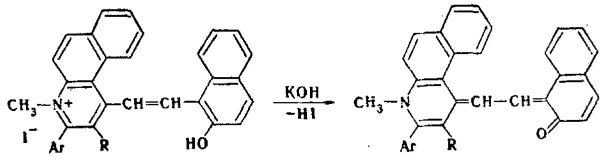
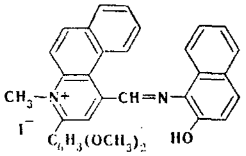


IIIa-g R = H; III hR = CH_3 IIIa-h

2-Hydroxy-5,6-benzostyryl derivatives of 3-arylbenzo[f]quinolinium salts were obtained by condensation [5] of 1-methyl- and 1,2-dimethyl-3-arylbenzo[f]quinolinium methiodides with 2-hydroxynaphthaldehyde. In contrast to hydroxystyrenes, the anhydro bases of which (III) can be isolated only by the action of alkali on the hydroxystyryl salt, hydroxyazomethine bases I are formed immediately in the reaction of the starting compounds. However, in addition to Ig, we also isolated hydroxyazomethine methiodide IV [UV spectrum, λ_{max} (log ε): 421 (4.24), 500 (3.93), and 694 nm (3.36)] by refluxing the reaction mixture:



IV

Green crystals of hydroxyazomethine base Ig are isolated under milder conditions (Table 1). When one drop of KOH solution is added to an alcohol solution of IV, the salt is converted to a base [λ_{max} 702 nm (log ε 3.34)], whereas, on the other hand, when an alcohol solution of azomethine Ig is acidified with acetic acid, it is converted to a salt [λ_{max} 425 nm (log ε 4.60)].

The dyes that we synthesized differ from the analogous compounds [1, 2] in that their absorption maxima are shifted to a considerable extent to the long-wave region of the spectrum. The bathochromic shift of the absorption bands is a consequence of the introduction of electron-donor substituents in the benzoquinoline fragment of the dye molecules. The steric hindrance that develops in this case leads to a decrease in the absorption intensity, particularly in the case of azomethine dyes. The azomethine and mercocyanine dyes have solvatochromic properties. The color of their solutions deepens on passing from ethanol to chloroform (negative solvatochromism) [1, 6]. In addition to the great similarity in the spectral and solvatochromic properties of the dyes – azomethines and merocyanines – some differences in their spectral characteristics are also observed. Replacement of the methylidyne group by a nitrogen atom in the chromophore of the dyes causes a bathochromic shift of the long-wave absorption bands in accordance with the Dewar–Knott rule [7, 8]. Thus, the longest-wave $\pi-\pi^*$ bands in the spectra of the azomethines are shifted bathochromically 33-56 nm in ethanol and 59-66 nm in chloroform (Tables 1 and 3).

It is known from the literature data that aromatic azomethines have photoconductor properties [9]. It seemed of interest to investigate the electrophotographic properties of the compounds obtained in this research. Maximum concentrations (up to 5 wt.%) were introduced into polymer matrices [poly(butyl methacrylate) or a polyorganosiloxane]. The samples were investigated under electrophotographic conditions by means of a dynamic electrometer with a vibrating probe. The method and apparatus for the investigation of the electrophotographic parameters of the layers are described in [10]. The compositions obtained from azomethines Ic-h introduced into poly(butyl methacrylate) at a layer thickness of 3 μ are charged up to 500-600 V (at a charge potential of 600 V), have a considerable dark decrease (200 V in 15 sec), and display weak sensitivity in the UV and visible regions. The layers in which azomethines Ia, b are located are charged to a great extent (500-600 V) and have an appreciable dark decrease, but even on the background of this decrease at concentrations of 1-1.3 wt.% have considerable photosensitivity in the UV and visible regions; this is apparent from Fig. 1 (curves 1-3). Compositions based on merocyanines IIIa-e and IIIh are charged up to 500-550 V and have a dark decrease of 10-80 V in 15 sec and appreciable photosensitivity in the visible region (curves 4 and 5 in Fig. 1). The layer containing IIIf is charged up to 250 V, has a slight dark decrease (10 V in 15 sec), and has sensitivity in the visible region (a light decrease of 80-100 V in 15 sec). The studies do not make it possible to draw a definite conclusion regarding the true value of the photoelectric sensitivity of the synthesized compounds. However, considering the appreciable photosensitivity of the compositions containing dyes in extremely low concentrations, one may assume high efficiency of photogeneration and transfer of charge carriers in Ib and IIIe.

TABLE 1. Azomethine Dyes (Ia-h)

Compound	Ar	mp, °C	Found, %			Empirical formula	Calc., %			λ_{max}, nm (lg ε)		Yield, %
			C	H	N		C	H	N	C_2H_5OH	CHCl	
Ia	C_6H_5	144—145	84,9	5,1	6,2	$C_{31}H_{22}N_2O$	84,9	5,0	6,4	703(4,13)	769(3,41)	33
Ib	p-$CH_3OC_6H_4$	154—156	81,8	5,1	6,0	$C_{32}H_{24}N_2O_2$	82,0	5,1	6,0	408(4,49) 700(4,47)	761(4,18)	53
Ic	3,4-$(OCH_2O)C_6H_3$	177—179	79,7	4,6	5,6	$C_{32}H_{22}N_2O_3$	79,6	4,5	5,8	407(4,08) 701(4,23)	772(3,45)	29
Id	p-FC_6H_4	154			6,4	$C_{31}H_{21}FN_2O$			6,2	722(3,66)	774(3,15)	44
Ie	p-ClC_6H_4	153—154	78,7	4,4	5,7	$C_{31}H_{21}ClN_2O$	78,7	4,4	5,9	722(3,54)	774(4,07)	53
If	p-BrC_6H_4	156	71,9	4,3	5,5	$C_{31}H_{21}BrN_2O$	71,9	4,0	5,4	718(3,83)	779(3,11)	34
Ig	3,4-$(CH_3O)_2C_6H_3$	160—161	79,5	5,3	5,8	$C_{33}H_{26}N_2O_3$	79,5	5,2	5,6	413(4,01) 703(4,08)	770(3,62)	32
Ih*	C_6H_5	148—150	84,7	4,7	6,0	$C_{32}H_{24}N_2O$	84,9	4,6	6,2	703(3,52)	773(3,52)	22

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*R = CH_3.

TABLE 2. Absorption Spectra of Azomethines IIa-h in Ethanol

Compound	λ_{max}, nm (log ε) (base)	λ_{max}, nm (log ε) (acetate)
IIa	703 (4,13)	403 (3,82); 507 (3,59)
IIb	408 (4,49); 700 (4,47)	417 (4,24); 504 (3,87)
IIc	407 (4,08); 701 (4,23)	420 (4,21); 493 (3,92)
IId	722 (3,66)	405 (4,15); 509 (3,95)
IIe	722 (3,54)	406 (4,09); 511 (3,85)
IIf	718 (3,83)	406 (4,15); 512 (3,90)
IIg	413 (4,01); 703 (4,03)	425 (4,60); 500 (shoulder)
IIh	703 (3,52)	400 (3,92); 510 (3,60)

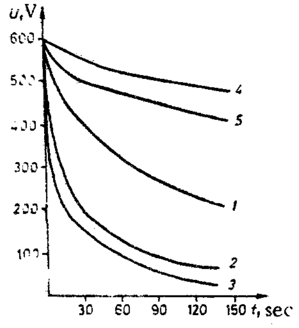

Fig. 1. Kinetics of the change in the surface potential of the layer obtained from the composition dye Ib (1.3%) + poly(butyl methacrylate): 1) in the dark; 2) in the UV region; 3) in the visible region; from the composition dye IIIe (3%) + polyorganosiloxane: 4) in the dark; 5) in the visible region.

TABLE 3. Merocyanines (IIIa-h)

Compound	Ar	mp, °C	Found, %		Empirical formula	Calc., %		λ_{max}, nm (log ε)	Yield, %
			C	H		C	H	(1) in C_2H_5OH; (2) in $CHCl_3$	
IIIa	C_6H_5	237—238	87,5	5,5	$C_{32}H_{23}NO$	87,8	5,3	(1) 474 (3,83) 670 (4,34) (2) 431 (3,56) 673 (4,20) 710 (4,30)	73
IIIb	p-$CH_3OC_6H_4$	235—236	81,6	5,8	$C_{33}H_{25}NO_2 \cdot H_2O$	81,6	5,8	(1) 471 (4,13) 666 (3,70) (2) 677 (4,17) 712 (4,30)	70
IIIc	3,4-(OCH_2O)C_6H_3	247—248	79,5	5,0	$C_{33}H_{23}NO_3 \cdot H_2O$	79,4	5,0	(1) 456 (3,83) 664 (3,78) (2) 670 (4,30) 710 (4,38)	37
IIId*	p-FC_6H_4	225			$C_{32}H_{22}FNO \cdot H_2O$			(1) 466 (3,40) 666 (3,62) (2) 439 (3,37) 670 (4,40) 707 (4,46)	90
IIIe	p-ClC_6H_4	227—228	75,8	5,2	$C_{32}H_{22}ClNO \cdot 2H_2O$	75,6	5,1	(1) 455 (3,24) 675 (3,32) (2) 434 (3,34) 672 (4,32) 708 (4,39)	61
IIIf	p-BrC_6H_4	233	71,9	4,4	$C_{32}H_{22}BrNO \cdot H_2O$	71,9	4,5	(1) 437 (3,34) 664 (3,34) (2) 444 (3,30) 675 (4,34) 713 (4,41)	84
IIIg	3,4-$(CH_3O)_2C_6H_3$	253	79,3	5,7	$C_{34}H_{27}NO_3 \cdot H_2O$	79,2	5,6	(1) 403 (4,09) 665 (4,02) (2) 673 (4,76) 714 (4,89)	43
IIIh†	C_6H_5	231—232	84,4	5,7	$C_{33}H_{25}NO \cdot H_2O$	84,4	5,7	(1) 477 (3,96) 666 (4,12) (2) 714 (4,02)	33

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*Found: N 2.8%. Calculated: N 2.9%.

†R = CH_3.

EXPERIMENTAL

The absorption spectra of ethanol and chloroform solutions of the dyes (c 10^{-4} M) were recorded with a Specord UV-vis spectrophotometer.

4-Methyl-3-arylbenzo[f]dihydroquinolylidene-1-(2-oxo-1-naphthylamines) (Ia-g). These compounds were obtained by the methods in [1, 2]. A mixture of equimolar amounts (1 mmole) of 1-methyl-3-arylbenzo[f]quinolinium methiodide and 1-nitroso-2-naphthol was dissolved by heating in ethanol, four to five drops of piperidine were added, and the mixture was heated at 80°C for 10 min. The resulting precipitate was removed by filtration and washed with water, alcohol, and ether. The dyes, which were recrystallized from acetone–chloroform (1 : 1), were obtained as green or green-violet needles (Table 1).

2,4-Dimethyl-3-phenylbenzo[f]dihydro-1-quinolylidene(2-oxo-1-naphthylamine) (Ih). This compound was similarly obtained from 1,2-dimethyl-3-phenylbenzo[f]quinolinium methiodide by adding two drops of acetic anhydride to the reaction mixture and refluxing on a water bath for 1-2 min.

4-Methyl-3-(3,4-dimethoxyphenyl)-1-(2-hydroxy-1-naphthylamine)benzo[f]quinolinidenium Iodide (IV). A 0.47-g (1 mmole) sample of 1-methyl-3-(3,4-dimethoxyphenyl)benzo[f]quinolinium methiodide and 0.18 g (1 mmole) of 1-nitroso-2-naphthol were dissolved by heating in 60 ml of ethanol, four drops of piperidine were added, and the mixture was refluxed on a water bath for 10 min. The precipitate was washed with alcohol and refluxed with benzene. Workup of the benzene solution yielded 0.1 g of the starting base. The benzene-insoluble material was crystallized from ethanol–acetone (1 : 1) to give 0.08 g (18%) of IV with mp 241-242°C as shiny red needles. Found: C 63.2; H 4.3; I 20.2%. $C_{33}H_{27}IN_2O_3$. Calculated: C 63.2; H 4.3; I 20.3%.

[4-Methyl-3-(p-methoxyphenyl)benzo[f]dihydro-1-quinolylidene]-(5,6-benzo-2-quino)ethane (IIIb). A 0.3-g (0.5 mmole) sample of 1-(2-hydroxy-5,6-benzostyryl)-3-(p-methoxyphenyl)benzo[f]quinolinium methiodide was dissolved by heating in ethanol, 15 ml of 10% aqueous KOH solution was added, and the mixture was heated on a water bath for 10 min. The resulting precipitate was removed by filtration, washed with water, alcohol, and ether, and crystallized from chloroform to give 0.16 g of green needles with a bronze luster.

The remaining merocyanines were similarly obtained (Table 3).

The samples for the investigation of the photoconductivity were prepared by the following method. A 0.1-g sample of poly(butyl methacrylate) or polyorganosiloxane was dissolved in 1 ml of the solvent (toluene, benzene, or tetrahydrofuran), and the dye (1-5 wt.%) was added. The solution was filtered, the filtrate was poured over an aluminum support, and the support was dried in air and in a vacuum desiccator. Samples with a layer thickness of $3 \pm 0.5\ \mu$ were selected. For the determination of the photoinduced decrease in the potential in the near-UV region, the samples were irradiated with a DRSh-250 lamp through a UFS-1 light filter with $W = 10^{-5}$ Wt/cm^2. A 400-Wt incandescent lamp with a water filter with a thickness of 10 cm and $W = 10^{-4}$ Wt/cm^2 was used in the visible region as the source of photoexcitation.

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ACETALS OF LACTAMS AND ACID AMIDES

XX.* SYNTHESIS OF HYDROGENATED DERIVATIVES OF INDOLE, QUINOLINE, AND 1H,1-BENZAZEPINE

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Hydrogenated derivatives of indole, quinoline, and 1H,1-benzazepine were synthesized by reaction of 1-methyl-2-benzoylmethylenepyrrolidine, -piperidine, and -hexahydroazepine with acryloyl chloride. Alkylation of 1-methyl-5-oxo-8-benzoyl-1,2,3,4,5,6,7,8-octahydroquinoline with triethyloxonium tetrafluoroborate and subsequent treatment with sodium ethoxide gave the corresponding acetal, the reaction of which with substituted anilines gave 1-methyl-5-arylimino-8-benzoyl-1,2,3,4,5,6,7,8-octahydroquinolines. The IR and PMR spectra of the compounds are presented.

Enamino ketones I-III, which were obtained by condensation of lactam acetals with acetophenone [2], are promising substrates for the synthesis of condensed heterocyclic compounds that are of interest in the search for biologically active substances. The present paper is devoted to a study of the reaction of enamino ketones I-III with acryloyl chloride (IV). The synthesis of cyclohexene derivatives [3, 4] from noncyclic enamino carbonyl compounds and chloride IV and the reaction of 1-methyl-2-ethylidenepyrrolidine with acrolein, which

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*See [1] for communication XIX.

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