DIMETHYLIDYNEMEROCYANINOCYANINES — SUBSTITUTED BENZIMIDAZOLE DERIVATIVES

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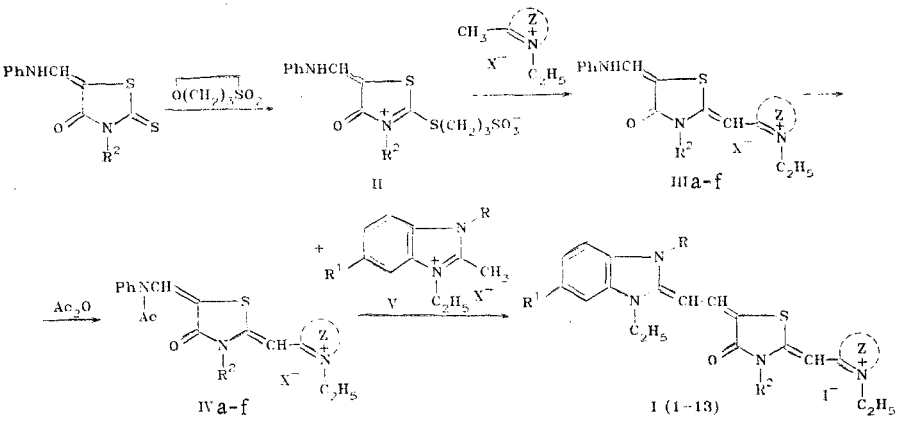
Dimethylidynemerocyaninocyanines — substituted benzimidazole derivatives — were synthesized. A decrease in the basicity of the benzimidazole ring with intensification of the electronegative properties of the substituent gives rise to a small (up to 10 nm) heightening of the color of the dyes obtained. The latter are rather effective spectral sensitizers of silver halide photographic emulsions.

Complex trinuclear dyes — merocyaninocyanines ("rhodacyanines") [1] — which, in addition to relatively high effectiveness, have component stability [2], continue to occupy an important position among spectral sensitizers that are currently being used in the manufacture of various sorts of motion picture and photographic materials. Although a significant number of publications have been devoted to the synthesis and investigation of the properties of this group of dyes, which differ with respect to the nature of the nitrogen-containing heterocyclic residues [2-5] and other structural elements [6-9], virtually no study has been devoted thus far to imidamerocyaninocyanines. At the same time, it is known that carbocyanine [10-12], merocyanine [13], and dimerocyanine [14] dyes with residues of substituted benzimidazoles are effective spectral sensitizers of silver halide photographic emulsions. In this connection it seemed of undoubted interest to synthesize and investigate the properties of imidadimethylidynemerocyaninocyanines with the I structure. We were able to obtain these dyes (Table 1) in satisfactory yields by condensation of acetanilinomethylene-substituted monomethylidynecyanines IV [15] with quaternary salts of substituted 2-methylbenzimidazoles V in dimethyl sulfoxide (DMSO) or absolute alcohol in the presence of triethylamine via the scheme presented below.



R = C_2H_5, Ph; R^1 = $COOC_2H_5$, CF_3SO_2, 2-benzothiazolyl; R^2 = C_2H_5, C_3H_5; Z are benzoxazole, 5-phenylbenzoxazole, benzothiazole, 5-methoxybenzothiazole, 4,5-diphenylthiazole, and 1-ethyl-5-trifluoromethylsulfonylbenzimidazole residues.

It should be noted that only traces of merocyaninocyanines I are formed in the reaction of monomethylidynecyanines III with quaternary salts V in a mixture of acetic anhydride, pyri-

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TABLE 1. Dyes I

Compound I[a]	Z	R'	Appearance	mp,[b] °C	λ_{max}, nm in C_2H_5OH ($\varepsilon \cdot 10^{-3}$)	Found, %			Empirical formula	Calc., %			Yield, % (method)
						C	H	N (S)		C	H	N (S)	
1	3-Ethyl-2-benzoxazolium	$COOC_2H_5$	Light-brown needles	270—271 (100)	577 (95)	53,1	5,0	7,8	$C_{31}H_{35}IN_4O_4S \cdot H_2O$	52,8	5,2	7,9	40 (A)
2	3-Ethyl-2-benzothiazolium	$COOC_2H_5$	Dark-green prisms	259—260 (113)	591 (86)	52,7	5,3	8,3	$C_{31}H_{35}IN_4O_3S_2$	53,0	5,0	8,0	51 (A)
3	3-Ethyl-5-methoxy-2-benzothiazolium	$COOC_2H_5$	Dark-brown prisms	263—265 (430)	594 (94)	51,5	5,2	7,2	$C_{32}H_{37}IN_4O_4S_2 \cdot H_2O$	51,2	5,2	7,5	63 (A)
4	3-Ethyl-4,5-diphenyl-2-thiazolium	$COOC_2H_5$	Brownish-green crystals	225—227 (60)	588 (77)	58,5	5,1	6,6	$C_{40}H_{41}IN_4O_3S_2$	58,8	5,0	6,9	20 (A)
5[c]	1,3-Diethyl-5-trifluoromethylsulfonyl-2-benzimidazolium	$COOC_2H_5$	Purple needles	247—249 (180)	547 (48)	—	—	(7,5)	$C_{34}H_{39}ClF_3N_5O_9S_2$	—	—	(7,8)	21 (A)
6	3-Ethyl-2-benzoxazolium	CF_3SO_2	Green prisms	202—204 (140)	578 (115)	46,5	4,2	—	$C_{29}H_{30}F_3IN_4O_4S_2$	46,6	4,0	—	54 (B)
7	3-Ethyl-2-benzothiazolium	CF_3SO_2	Bronze prisms	215—217 (160)	592 (102)	45,7	4,3	7,1	$C_{29}H_{30}F_3IN_4O_3S_3$	45,7	3,9	7,3	42 (B)
8	3-Ethyl-5-methoxy-2-benzothiazolium	CF_3SO_2	Violet prisms	245—247 (215)	594 (104)	44,3	3,9	6,6	$C_{30}H_{32}F_3IN_4O_4S_3 \cdot H_2O$	44,4	4,2	6,9	35 (B)
9	3-Ethyl-5-phenyl-2-benzoxazolium	CF_3SO_2	Green crystals	265—267 (320)	582 (137)	—	—	(7,8)	$C_{35}H_{34}F_3IN_4O_4S_2$	—	—	(7,8)	40 (B)
10	3-Ethyl-4,5-diphenyl-2-thiazolium	CF_3SO_2	Green prisms	232—234 (220)	589 (105)	51,8	4,0	6,1	$C_{38}H_{36}F_3IN_4O_3S_3$	52,0	4,1	6,3	50 (B)
11	3-Ethyl-2-benzoxazolium	2-Benzothiazolyl	Green crystals	266—268 (550)	588 (93)	57,8	4,8	8,4	$C_{39}H_{34}IN_5O_2S_2 \cdot H_2O$	57,6	4,4	8,6	25 (A)
12	3-Ethyl-2-benzothiazolium	2-Benzothiazolyl	Dark-green prisms	231—232 (500)	602 (94)	56,7	4,5	—	$C_{39}H_{34}IN_5OS_3 \cdot H_2O$	56,5	4,3	—	39 (A)
13	3-Ethyl-4,5-diphenyl-2-thiazolium	2-Benzothiazolyl	Dark-brown prisms	263—265 (1200)	599 (124)	—	—	(10,3)	$C_{48}H_{40}IN_5OS_3$	—	—	(10,4)	35 (A)

[a] In compounds 1-10 R = C_2H_5, in compounds 11-13 R = C_6H_5, in compounds 4, 10, and 13 R^2 = C_3H_5, and in the remaining compounds R^2 = C_2H_5. [b] The amount of methanol in milliliters per gram used for the recrystallization of the dye is indicated in parentheses. [c] The perchlorate.

dine, and triethylamine by the method in [16]. This is evidently associated with the decreased reactivity of the methyl group in quaternary salts V.

In the preparation of betaines II we used 1,3-propanesultone as the alkylating agent instead of the dialkyl sulfates and alkyl esters of arenesulfonic acids that have been previously used for this purpose. The synthesis of monomethylidynecyanines III on the basis of these betaines excludes the formation of highly volatile and toxic alkyl mercaptans, and this substantially improves the working conditions and prevents contamination of the atmosphere in the preparation of III on an industrial scale [17]. The acetylation of monomethylidynecyanines III was realized in acetic anhydride in the presence of triethylamine with moderate heating [15, 18].

As one should have expected [3], a decrease in the basicity of the benzimidazole ring with intensification of the electronegative properties of the R^1 substituent* gives rise to a small (up to 10 nm) heightening of the color of I. As in the case of imida- and other carbocyanine dyes [19], a decrease in the polarity of the solvent leads to a shift of the absorption maxima of imidamerocyaninocyanines to the long-wave part of the spectrum. Thus the absorption maxima of dyes I-2 and I-7 are shifted from 591 nm in alcohol to 601 nm in chloroform and 609 nm in benzene, and the absorption maxima of dye I-12 are shifted from 602 nm in alcohol to 611 nm in chloroform and 612 nm in benzene.

The synthesized merocyaninocyanines are rather effective spectral sensitizers of silver halide photographic emulsions in the zone of the spectrum up to 660 nm with maximum sensitization at 600-630 nm.

EXPERIMENTAL

3-Ethyl-5-phenyl-2-[(5-anilinomethylene-4-oxo-3-ethylthiazolidin-2-ylidene)methyl]benzoxazolium Ethylsulfate (IIIb). A mixture of 0.77 g (2 mmole) of 3-(3-ethyl-4-oxo-5-anilinomethylene-1,3-thiazol-2-inia-2-thio)propanesulfonate, 0.73 g (2 mmole) of 2-methyl-5-phenyl-3-ethylbenzoxazolium ethylsulfate, 40 ml of anhydrous chloroform, and 0.42 ml (3 mmole) of triethylamine was refluxed for 5.5 h and allowed to stand at 20°C for 12-15 h. The resulting precipitate was removed by filtration, washed on the filter with 2 ml of chloroform, and refluxed with 5 ml of absolute ethanol to give 0.63 g (54%) of orange prisms with mp 295-300°C (dec.) and λ_{max} (alcohol) 476 nm (ε 65,000). Found: S 10.9%. $C_{30}H_{28}N_3O_6S_2$. Calculated: S 10.9%.

3-Ethyl-5-phenyl-2-[(5-acetanilinomethylene-4-oxo-3-ethylthiazolidin-2-ylidene)methyl]-benzoxazolium Ethylsulfate (IVb). A mixture of 0.69 g (1.2 mmole) of IIIb and 2.4 ml of acetic anhydride was heated at 60°C and stirred for 5 min, after which 0.34 ml (2.4 mmole) of triethylamine was added, and the mixture was stirred at the same temperature for another 10 min and allowed to stand at 20°C for 12-15 h. Ether (10 ml) was added, and the resulting precipitate was removed by filtration and washed successively on the filter with 0.4 ml of a mixture of alcohol with ether (1:1), 0.02 ml of dry acetone, and 1 ml of ether to give 0.76 g (100%) of a product with mp 246-248°C. Recrystallization from ethanol (1:120) gave 0.51 g (67%) of dark-yellow plates with mp 248-251°C and λ_{max} (alcohol) 440 nm (ε 69,000). Found: S 9.8%. $C_{32}H_{30}N_3O_7S_2$. Calculated: S 10.1%.

1,3-Diethyl-5-trifluoromethylsulfonyl-2-[(5-acetanilinomethylene-4-oxo-3-ethylthiazolidin-2-ylidene)methyl]benzimidazolium Perchlorate (IVf). A mixture of 1.53 g (2.3 mmole) of 1,3-diethyl-5-trifluoromethylsulfonyl-2-[(5-anilinomethylene-4-oxo-3-ethylthiazolidin-2-ylidene)methyl]benzimidazolium perchlorate [17] and 2.25 ml of acetic anhydride was heated with stirring at 50°C for 5 min, after which 0.64 ml (4.6 mmole) of triethylamine was added, and the mixture was allowed to stand at 20°C for 2 h. Absolute ether (20 ml) was added to the resulting precipitate, and the latter was triturated with the ether, removed by filtration, and washed on the filter with another 20 ml of ether to give 1.38 g (100%) of a product with mp 195-197°C. Recrystallization from propyl alcohol (1:220) gave 0.80 g (58%) of light-brown prisms with mp 213-216°C and λ_{max} (alcohol) 348 and 310 nm (ε 49,000 and 46,000). Found: Cl 5.3%. $C_{27}H_{28}ClF_3N_4O_8S_2$. Calculated: Cl 5.2%.

3-Ethyl-2-{[5-1-R-3-ethyl-5-R^1-benzimidazolin-2-ylidene)ethylidene-4-oxo-3-R^2-thiazolidin-2-ylidene]methyl}azolium Iodides (Imidamerocyaninocyanines I, Table 1). These compounds were obtained by heating 0.25 mmole of the corresponding monomethylidynecyanine IV and 0.25

*Hammett σ_p constants: 0.44 for 2-benzothiazolyl, 0.52 for $COOC_2H_5$, and 0.96 for CF_3SO_2.

mmole of quaternary salt V in 1.5-3 ml of dimethyl sulfoxide (method A) or in 1.5 ml of absolute ethanol (method B) in the presence of 0.3-0.37 mmole of triethylamine for 20-30 min at 100-105°C (bath temperature), after which 3 ml of a 10% aqueous solution of potassium iodide heated to 70°C (dyes 2-4, 6-11, and 13) was added, and the mixture was allowed to stand for 12-16 h in a refrigerator (dyes 3 and 13) or at 20-25°C (dyes 2, 4, and 6-11). For the isolation of dyes 1 and 12 the reaction solution was cooled to 20-25°C, 1.5 ml of alcohol was added, and the mixture was maintained at 4-8°C for 1.5-2 h. The liberated dyes were removed by filtration, washed successively on the filter with 5-7 ml of water, 0.5-1 ml of alcohol, and 2-5 ml of ether, and crystallized from alcohol. Dyes 11 and 13 were washed by refluxing with 30 and 10 ml of alcohol, after which they were also crystallized from alcohol.

For the isolation of dye 5, 3 ml of a 10% aqueous solution of sodium perchlorate heated to 70°C was added to the hot reaction solution, and the mixture was allowed to stand at 20-25°C for 1 h. The liberated resinous precipitate was removed by filtration, washed on the filter with 30 ml of water, and triturated with 5 ml of water. The solid material was removed by filtration, washed with 30 ml of water, dried, and refluxed with 12 ml of alcohol. The undissolved residue was removed by filtration, washed on the filter with 0.5 ml of alcohol and 5 ml of ether, and recrystallized from alcohol.

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