UNSYMMETRICAL INDOLODIMETHYLIDYNECYANINES AND THEIR PROPERTIES

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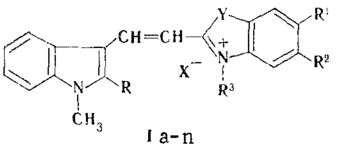
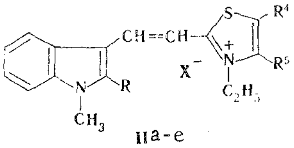
New unsymmetrical dimethylidynecyanines with various substituents in the heterocyclic rings were obtained by condensation of 1-methyl-2-arylindoles that contain a formyl group in the 3 position with quaternary salts of 2-methyl-substituted benzoxazoles, benzothiazoles, 3,3-dimethylindolenines, and benzoselenazoles in acetic anhydride by heating in the presence of p-toluenesulfonic acid. Unsymmetrical dimethylidynecyanines with residues of substituted thiazoles were similarly synthesized. The spectral, polarographic, and photographic characteristics of the dyes obtained were studied. It is shown that, depending on their structure, they absorb in different zones of the spectrum and can be used for the spectral sensitization of direct positive recording materials to various parts of the spectrum.

Unsymmetrical dimethylidynecyanines that are derivatives of 2-aryl-3-indoles are known as spectral sensitizers of direct positive silver halide photographic materials [1-3]. In the search for effective spectral sensitizers for such materials it seemed of interest to synthesize new dimethylidynecyanines that are derivatives of 1-alkyl-2-arylindoles with residues of heterocyclic bases that contain various substituents and to investigate their photographic effectiveness when they are introduced into direct positive emulsion photosensitive layers.

In this paper we describe the synthesis and study of the spectral, polarographic, and photographic characteristics of a number of new unsymmetrical indolodimethylidynecyanines with structures I and II (the R—R^5 radicals are presented in Table 1):



I a-n



IIa-e

Dyes with the I structure were obtained by condensation of 1-methyl-2-aryl-3-formylindoles with quaternary salts of 2-methyl-substituted benzoxazoles, benzothiazoles, benzoselenazoles, or 3,3-dimethylindolenines in acetic anhydride by heating in the presence of p-toluenesulfonic acid.

Cyanines with the II structure were synthesized similarly by means of quaternary salts of substituted thiazoles.

The absorption spectra of the synthesized dyes in ethanol were recorded (Table 1).

It follows from the data in Table 1 that the synthesized dimethylidynecyanines that are derivatives of 1-methyl-2-arylindoles absorb in different parts of the spectrum; this is due to differences in their structures in conformity with the nature of the heteroresidues and the substituents in them. Among the dyes with the I structure, the cyanines with a benzoxazole residue absorb in the shortest-wave region of the spectrum. The selenocyano- and nitro-substituted indolothiadimethylidynecyanines absorb in virtually the same spectral zone. This is also characteristic for the dyes with nitroindolenine residues. The cyanines with benzoselenazole residues are somewhat more deeply colored than the analogous benzothiazole derivatives; this is known to be characteristic for symmetrical and unsymmetrical trimethylidynecy-

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TABLE 1. Spectral and Polarographic Characteristics of Unsymmetrical Indolodimethylidynecyanines I and II

Compound	R	Y	R^1	R^2	R^3	R^4	R^5	X	λmax (in ethanol), nm	$\varepsilon_{max} \times 10^{-4}$ nm	$E_{1/2}$Ox, V	$-E_{1/2}^{Red}$, V
Ia	C_6H_5	O	H	Br	C_2H_5	—	—	I	480	3,85	0,90	0,87
Ib	C_6H_5	S	H	4-Cl	C_2H_5	—	—	I	506	5,6	0,60	0,64
Ic	C_6H_5	S	SeCN	H	C_2H_5	—	—	Br	516	4,45	—	—
Id	p-$CH_3C_6H_4$	S	SeCN	H	C_2H_5	—	—	Br	520	3,8	1,22	0,64
Ie	p-BrC_6H_4	S	SeCN	H	C_2H_5	—	—	Br	516	4,05	1,26	0,57
If	H	S	NO_2	H	C_2H_5	—	—	I	518	3,9	1,20	0,62
Ig	C_6H_5	S	NO_2	H	C_2H_5	—	—	Br	520	4,85	0,95	0,60
Ih	p-$CH_3C_6H_4$	S	NO_2	H	C_2H_5	—	—	Br	524	3,9	0,90	0,65
Ii	p-BrC_6H_4	S	NO_2	H	C_2H_5	—	—	Br	520	5,35	0,96	0,58
Ij	H	$C(CH_3)_2$	NO_2	H	CH_3	—	—	p-$H_3CC_6H_4SO_3$	524	4,8	1,40	0,70
Ik	C_6H_5	$C(CH_3)_2$	NO_2	H	CH_3	—	—	p-$H_3CC_6H_4SO_3$	527	7,0	1,35	0,66
Il	C_6H_5	Se	NO_2	H	C_2H_5	—	—	p-$H_3CC_6H_4SO_3$	532	4,55	0,98	0,68
Im	C_6H_5	Se	NO_2	H	C_2H_5	—	—	Br	530	5,2	—	—
In	p-BrC_6H_4	Se	NO_2	H	C_2H_5	—	—	p-$H_3CC_6H_4SO_3$	528	5,1	1,02	0,64
IIa	C_6H_5	—	—	—	—	$COOC_2H_5$	CH_3	I	495	4,5	1,30	0,80
IIb	p-$CH_3C_6H_4$	—	—	—	—	$COOC_2H_5$	CH_3	I	490	3,0	1,23	0,85
IIc	p-BrC_6H_4	—	—	—	—	$COOC_2H_5$	CH_3	I	494	4,45	1,26	0,78
IId	C_6H_5	—	—	—	—	COOH	COOH	I	504	2,8	0,60	0,75
IIe	C_6H_5	—	—	—	—	2H	2H	I	370	2,33	0,93	1,35

anines [4]. Thus the dyes with I and II structures, depending on their structure, can be used for sensitization of direct positive materials to various zones of the spectrum. In particular, cyanines I are suitable for their spectral sensitization chiefly to the green zone of the spectrum.

The redox and sensitizing properties of the compounds obtained were studied in comparison with phenosafranin [5] — the well-known sensitizer of direct positive photographic materiial. Their oxidation and reduction were studied with an LP-7 recording polarograph in acetonitrile with 0.1 mole/liter LiCl and 0.1 mole/liter $NaClO_4$ as the base electrolytes. The oxidation half-wave potentials were measured with rotating platinum glass graphite disk electrodes (ω = 1600 rpm, d = 3 mm), and the reduction half-wave potentials were measured with a dropping mercury electrode (m = 2.3 mg/sec and t = 3.7 sec when E = −0.80 V) relative to a saturated calomel electrode.

Solutions of the dyes with concentrations of $5 \cdot 10^{-5}$ to $1 \cdot 10^{-4}$ mole/liter were investigated. The results obtained are presented in Table 1.

It follows from the data in Table 1 that the $E_{1/2}^{Ox}$ and $E_{1/2}^{Red}$ values of the dyes vary as a function of the nature of the heterocyclic residue and the character of the substituents in it. The introduction of a bromine atom in the para position of the phenyl group facilitates reduction and hinders oxidation of the dyes: the $E_{1/2}^{Red}$ values decrease, while the $E_{1/2}^{Ox}$ values increase. The character of the effect of methyl groups in these positions on the $E_{1/2}^{Red}$ and $E_{1/2}^{Ox}$ values is just the opposite. The introduction of a phenyl group in the 2 position of the indole heteroresidue of the dimethylidynecyanines leads to a decrease in their $E_{1/2}^{Red}$ and $E_{1/2}^{Ox}$ values. The dyes that contain a nitro group in the benzoselenaole residue are characterized by greater reduction and oxidation potentials than the corresponding nitro derivatives with a benzothiazole residue. This is also characteristic, and to a greater degree, for dimethylidynecyanines with a nitroindolenine residue. Greater values of the oxidation potentials than for the corresponding nitro derivatives are characteristic for the compounds with an SeCN group in the benzothiazole residue vis-à-vis close $E_{1/2}^{Red}$ values.

Photographic tests were made on a monodispersed emulsion with cubic single crystals (average grain size 0.2 μm). The dyes were introduced into the fused emulsion at pH 6.5 and pBr* 3.0 at 40°C. Samples of the photographic materials were exposed with an FSR-41 sensitometer for 30 sec at a color temperaturre of 2850°K and for 5 min behind a red light filter (sensitometric). The sensitograms were subjected to chemical-photographic treatment in a UP-2 developer for 1 min at 20°C. The spectral sensitivity was determined by exposing samples of the film with an ISP-73 spectrosensitometer; the maximum spectral sensitivity to the light source was at 3200°K according to the spectrosensitograms. The suitability of the ma-

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*The pBr value is the negative logarithm of the bromide ion concentration in the emulsion.

TABLE 2. Characteristics of the Photosensitive Layers Containing Dyes I

Dye	Concn. in mg per mole of AgHal	$E_{1/2}$Ox	$E_{1/2}$Red	$S_{0,9}$ [a]	γ [b]	D_{min} [c]	D_{max} [c]	λ_{max} of sensitization, nm	Boundary of the sensitization zone, nm
Ii	200	0,96	−0,58	0,093	5,0	0,05	3,0	560	625
Ih	100	0,90	−0,65	0,080	4,8	0,06	3,0	560	625
Ik	120	1,35	−0,66	0,050	4,2	0,10	3,0	560	625
Phenosafranin	100		−0,72	0,008	4,2	0,12	3,0	545	600

[a] The $S_{0.9}$ value is the reciprocal of the exposure in ergs per square centimeter to obtain a density of the photographic image of 0.9. [b] The γ value is the coefficient of contrast of the photographic material. [c] The D_{min} and D_{max} values are the minimum and maximum densities in parts of the image, respectively.

TABLE 3. Characteristics of the Photosensitive Layers Sensitized by Dyes I and II in Conjunction with a 4,4'-Dipyridylium Salt

Dye	$E_{1/2}$Ox	$E_{1/2}$Red	$S_{0,9}$	γ	D_{min}	D_{max}
Ig	0,95	−0,60	0,16	4,0	0,07	2,45
Ih	0,90	−0,65	0,15	3,5	0,07	2,47
Ii	0,96	−0,58	0,20	4,0	0,06	2,29
Il	0,98	−0,68	0,12	3,4	0,07	2,45
IIa	1,30	−0,80	0,10	5,2	0,07	3,0
IIb	1,23	−0,85	0,10	4,3	0,07	2,91

terials for work under nonactinic illumination conditions was found by their exposure for 10 min with a laboratory projector with a 25-W lamp shielded by a No. 107 red light filter at a distance of 1 m from the plane of the film. The results of the studies are presented in Tables 2 and 3.

It is known that less negative cathode potentials are characteristic for typical desensitizers such as phenosafranin than for sensitizing cyanine dyes [5].

The data presented in Table 2 show that the photographic sensitivities of materials that contain dyes Ii, Ih, and Ik considerably exceed the photographic sensitivities of layers with phenosafranin, which corresponds to the low values of their cathode potentials. Benzothiazole derivative Ii, which contains a bromophenyl group in the 2 position of the indole ring, is more effective than the analogous dye with a 2-(p-tolyl) group (Ih). The dyes with nitro-3, 3-dimethylindolenine (Ik) and nitrobenzoselenazole (I*l*) residues are inferior to the benzothiazole derivative (Table 3). The photographic effectiveness of dyes I and II is increased appreciably when they are used in conjunction with 4,4'-dipyridylium salts.

Dyes IIa,b, which are 5-carbethoxythiazole derivatives (Table 3), display lower effectiveness than the dimethylidynecyanines with the I structure. The photographic characteristics of direct positive materials when the same dimethylidyneindolocyanines are used as electron acceptors also depend to a significant extent on the composition of the developer and the developing conditions.

EXPERIMENTAL

The dyes with the I structure were obtained by heating a mixture of 1 mmole of 1-methyl-2-aryl-3-formylindole with 1 mmole of the quaternary salt of a methyl-substituted heterocyclic base (benzoxazole, benzothiazole, 3,3-dimethylindolenine, benzoselenazole, and their derivatives) in 5-10 ml of acetic anhydride for 5-10 min with gentle refluxing in the presence of 1 mmole of p-toluenesulfonic acid. After cooling, the reaction mixture was diluted with ether, and the ether layer was decanted. The residue was washed with ether and dissolved by heating in ethanol. An equal volume of a hot 10% solution of potassium iodide or bromide was added to the solution, and the mixture was cooled and filtered. The dyes were isolated by dilution of the cooled reaction mixtures with ether and were purified by recrystallization from ethanol.

TABLE 4. Characteristics of the Dyes with Structures I and II

Compound	mp, °C	Found, %			Empirical formula	Calc., %			Yield, %
		Br	N	S		Br	N	S	
Ia[a]	201—202	—	—	—	$C_{26}H_{22}BrIN_2O$	—	—	—	3
Ib	140—141	—	4,9	5,6	$C_{26}H_{22}ClIN_2S$	—	5,0	5,7	4
Ic	183—184	13,7	7,1	—	$C_{27}H_{22}BrN_3SSe$	13,8	7,2	—	25
Id	189—190	13,3	7,0	—	$C_{28}H_{25}BrN_3SSe$	13,5	7,1	—	7
Ie	187—188	24,1	6,2	—	$C_{27}H_{21}Br_2N_3SSe$	24,3	6,4	—	5
If	235—236	—	8,4	6,4	$C_{20}H_{18}IN_3O_2S$	—	8,5	6,5	4
Ig	207—208	—	7,9	6,3	$C_{26}H_{22}BrN_3O_2S$	—	8,1	6,2	10
Ih	181—182	—	7,7	5,6	$C_{27}H_{24}BrN_3O_2S$	—	7,8	5,9	51
Ii	220—221	—	6,9	5,5	$C_{26}H_{21}Br_2N_3O_2S$	—	7,0	5,3	52
Ij	237—238	—	7,8	5,9	$C_{29}H_{29}N_3O_5S$	—	7,9	6,0	35
Ik	198—199	—	6,9	5,3	$C_{35}H_{33}N_3O_5S$	—	6,9	5,3	34
Il[b]	192—193	—	6,4	—	$C_{33}H_{29}N_3O_5SeS$	—	6,4	—	23
Im	238—239	13,9	7,2	—	$C_{26}H_{22}BrN_3O_2Se$	14,1	7,4	—	46
In	214—215	10,7	5,6	—	$C_{33}H_{28}BrN_3O_5SeS$	10,8	5,7	—	20
IIa	197—198	—	5,2	5,7	$C_{26}H_{27}IN_2O_2S$	—	5,0	5,7	39
IIb	126—127	—	5,0	5,7	$C_{27}H_{29}IN_2O_2S$	—	4,9	5,6	48
IIc	122—123	—	4,2	5,2	$C_{26}H_{26}BrIN_2O_2S$	—	4,4	5,0	20
IId	107—108	—	5,0	5,6	$C_{24}H_{21}IN_2O_4S$	—	5,1	5,7	10
IIe	149—150	—	6,0	6,9	$C_{21}H_{18}IN_2S$	—	6,1	7,0	14

[a] Found: C 53.3; H 3.8%. Calculated: C 53.3; H 3.8%. [b] Found: C 60.1; H 4.8%. Calculated: C 60.2; H 4.4%.

The dyes with the II structure were similarly obtained by means of quaternary salts of substituted thiazoles.

The results of analysis and the characteristics of the synthesized dimethylidynecyanines I and II are presented in Table 4.

The absorption spectra of the dyes in ethanol were recorded with a Hitachi spectrophotometer.

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