SYNTHESIS AND PROPERTIES OF 8-PHENYLINDOLO-3,3'-TRIMETHINECYANINES

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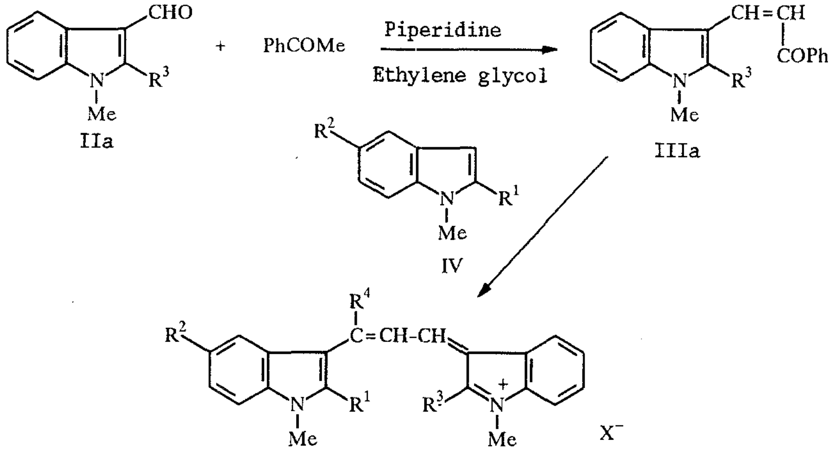
The condensation of 1-methyl-2-aryl-3-(2-benzoylvinyl)indoles with substituted indoles in acetic anhydride in the presence of a mineral acid afforded 8-phenylindolo-3,3'-trimethinecyanines. Their spectral, polarographic, and photographic properties were studied.

Among cyanine dyes of derivatives of 2-arylindoles were previously found effective spectral sensitizers of direct positive silver halide photoemulsions [1, 2].

Continuing the investigation of the properties of indolocyanine dyes with the object of finding more effective sensitizers, we obtained the 8-phenylindolotrimethinecyanines (Ia-e). The dyes were synthesized by the reaction of 1-methyl-2-R^3-3-(2-benzoylvinyl)indole (IIIa) with the corresponding indoles (IV) in acetic anhydride in the presence of a mineral acid:



Ia-e

I a R^1=R^2=H, R^3=R^4=Ph, X=Br; b R^1=R^3=R^4=Ph, R^2=H, X=ClO_4; c R^1=p-MeC_6H_4, R^2=H, R^3=R^4=Ph, X=Br; d R^1=p-BrC_6H_4, R^2=H, R^3=R^4=Ph, X=Br; e R^1=R^3=R^4=Ph, R^2=NO_2, X=Br;
IIa-IIIa R^3=Ph

The 1-methyl-2-R^3-3-(benzoylvinyl)indole (IIIa) was obtained, in its turn, by the condensation of the 1-methyl-2-R^3-3-formylindole (IIa) with acetophenone in ethylene glycol on heating the mixture in the presence of piperidine [3].

Table 1 presents the characteristics of the absorption spectra of the dyes (Ia-e) in the 5:1 mixture of nitromethane—acetic acid and their polarographic potentials.

The data of Table 1 show that the 8-phenylindolotrimethinecyanines (Ia-e) have deeper absorption than the unsubstituted (Ih) (R^4 = H, R^1 = R^3 = C_6H_5) and the 8-methyl-substituted (Ii) (R^1 = R^3 = C_6H_5, R^4 = CH_3) dyes [1, 2]. The absorption maximum of the 8-phenylindolotrimethinecyanine (Ia), containing a phenyl group at the position 2 of only one of the indole hetero-residues, is situated at the spectral region of shorter wavelength than that of the compounds (Ib-g). The methyl group in the p-position of the 2-phenyl groups has virtually no influence on the position of the absorption maximum of these dyes [cf. (Ic) and (If) (R^1 = R^3 = p-$CH_3C_6H_4$, R^4 = C_6H_5)]. The same is also characteristic of the compound (Ie) with a nitro group at the position 5 of the indole ring. The introduction of the bromine atom to the p-position of the phenyl group of only one of the indole residues in the indolocyanine (Id) leads to a bathochromic shift of its absorption maximum to the extent of 8 nm by comparison with the dye (Ig) (R^1 = R^3 = p-BrC_6H_4, R^4 = C_6H_5) of symmetrical structure [2].

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TABLE 1. Spectral and Polarographic Properties of the Indolotrimethinecyanines (Ia-e), and Photographic Characteristics of the Materials

Compound	Empirical formula	mp, °C	Absorption maximum in the 5:1 mixture of nitromethane-acetic acid		Polarographic potentials		Photographic characteristics of the materials				
			λ_{max}, nm	$\varepsilon_{max} \cdot 10^4$	$E_{\frac{1}{2}}^{Ox}$, V	$-E_{\frac{1}{2}}^{Red}$, V	time of development	$S_{0,85}$	γ	D_{max}	D_{min}
Ia	$C_{33}H_{27}BrN_2$	173...174	620	4,3	0,98	0,65	1	0,025	4,4	4,30	0,36
							3	0,014	5,0	4,20	0,56
Ib	$C_{33}H_{31}ClN_2O_4$	254...255	626	11,0	1,0	0,64	1	0,30	8,13	4,16	0,04
							3	0,27	9,33	4,63	0,04
Ic	$C_{45}H_{39}BrN_2$	179...180	628	10,2	1,0	0,64	1	0,40	6,7	3,65	0,04
							3	0,33	7,7	3,22	0,04
Id	$C_{33}H_{32}Br_2N_2$	182...183	636	15,9	0,97	0,67	1	0,37	7,3	3,84	0,04
							3	0,30	7,7	3,80	0,04
Ie	$C_{33}H_{30}BrN_3O_2$	189...190	628	10,6	0,99	0,65	1	0,19	10,4	4,10	0,04
							3	0,14	10,0	4,65	0,06
V							1	0,06	1,3	1,18	0,04
							3	0,03	3.8	2.92	0.03

It can be seen from Table 1 that these dyes are characterized by high $E_{1/2}^{Ox}$ potentials and the positive sign of the sum of the anode and cathode half-wave potentials. The reduction potential $E_{1/2}^{Red}$ is thereby less negative than —1.0-1.06 V, and the oxidation potential $E_{1/2}^{Ox}$ is greater than 0.4 V [4, 5], in agreement with which the synthesized indolo-3,3′-trimethinecyanines may show high photographic effectiveness as spectral sensitizers in direct positive silver halide emulsions.

Investigations of their photographic properties (Table 1) is presented in comparison with the known electron-acceptor compound N,N′-dimethyl-1,1′-dipyridylium dichloride (V), the $E_{1/2}^{Ox}$ and $E_{1/2}^{Red}$ of which comprise 1.5 and —0.64 V, correspondingly. It follows from the results obtained that the photomaterials containing the indolotrimethinecyanines (Ib-e) are characterized by higher values of the light sensitivity (S), coefficient of contrast (γ), and the maximal optical density of the images (D_{max}) than is the case for the photolayers with the compound (V). The dye (Ia) is significantly inferior to the sensitizer (V) in its photographic effectiveness, and possesses higher masking capacity. Consequently, the 8-phenylindolotrimethinecyanines (Ib-e) synthesized are mainly effective spectral sensitizers of direct positive photographic emulsions.

EXPERIMENTAL

The absorption spectra of the dyes in the visible region were measured on the SF-10 spectrophotometer. Polarographic potentials were determined according to the method of [1]. The structure of the substances obtained was confirmed by the data of the elemental analysis.

1-Methyl-2-phenyl-3-(2-benzoylvinyl)indole (IIIa, $C_{24}H_{19}NO$). The mixture of 5 g (0.021 mole) of 1-methyl-2-phenyl-3-formylindole (IIa), 2.52 g (0.021 mole) of acetophenone, 21 ml of ethylene glycol, and 1 ml of piperidine is heated for 50 min at 160-180°C; the mixture is cooled prior to the addition of 21 ml of water and 3 ml of acetic acid. The precipitated residue is filtered off and recrystallized from ethyl alcohol. It comprises yellow prisms with mp 157-158°C. The yield of compound (IIIa) is 2.9 g (48.5%).

8-Phenylindolo-3,3′-trimethinecyanines (Ia-e). To the mixture of 0.15 g (0.4 mmole) of 1-methyl-2-phenyl-3-(2-benzoylvinyl) indole (IIIa), 0.4 mmole of 1-methyl-2-R^1-5-R^2-indole, and 10 ml of acetic anhydride at 20°C is added, dropwise, the solution of 0.1 ml of perchloric acid of hydrobromic acid in 3 ml of acetic anhydride; the mixture is stirred for 3 h at 20°C prior to the dilution with 200 ml of ether. The residue is filtered off and washed with ether. The dye is purified by reprecipitation from acetic anhydride. The yield of (Ia-e) is 65-90%.

Photographic Emulsion. The photoemulsion is obtained by the method of controlled two-jet emulsification at pBr = 3.1 ± 0.1 and pH 5.5. The surface of the emulsion microcrystals is masked by stannous chloride and chloroauric acid at 70°C. The content of the dye (I) in the emulsion is 100 mg/mole of AgBr. To the sensitized emulsion is added a wetting agent and a tanning agent, after which it is irrigated onto a transparent film of cellulose triacetate to provide a layer with the content of 2.5 g/m^2 of metallic silver. The photomaterial is exposed for 30 sec at the color temperature of 2850 K on the FSR-41 sensitometer.

The chemicophotographical treatment of the sensitograms is performed by the development in the UP-2 for 1 and 3 min at 20°C, washing with water for 15 sec, and fixation in a 25% solution of sodium thiosulfate. The optical density of the fields of the sensitograms is measured on the DFÉ-10 densitometer.

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