## CYANINE DYES WITH AN ISOINDOLENINE RING

## IN THE CHROMOPHORE

A. Ya. Il'chenko and I. D. Radchenko

2-[3-(3-Methyl-2-benzothiazolinylidenyl)-1-methylisoindolinylidenyl]methyl-3-methylbenzothiazolium perchlorate was obtained by the condensation of 2-methylbenzothiazole methylmethosulfate with 1,1,3-trichloroisoindolenine. Similar dyes of the pyridine and quinoline series were also synthesized. The absorption bands of the cyanine dyes with an isoindolenine ring in the chromophore are shifted by 30 nm to the shortwave region in comparison with the corresponding dicarbocyanines. Acids protonate the dyes at the isoindolenine ring to form compounds with two conjugated chromophores. Condensation of 1,1,3-trichloroisoindolenine with N-substituted rhodanines yields 3-substituted 5-[3-(3-methyl-4-hydroxythiazoline-2,5-thionyl)-1-isoindolinylidene]rhodanines. Alkylation and hydrolysis of the Nmethyl substituted dye yields 5-[3-(3-methyl-4-hydroxy-5-thiazolin-5-onyl)isoindolinylidene-1]-3-methylthiazolidine-2,4-dione.

We have synthesized cyanine dyes which contain an isoindolenine ring in the chromophore by the reaction of quaternary salts of nitrogen heterocycles with an active methyl group or of the methylene bases obtained from them with 1,1,3-trichloroisoindolenine (II). Dye III ( $\lambda_{max}$  623 nm) was obtained from 2methylbenzothiazole methylmethosulfate (I).



Dyes VI and IX, which contain pyridine and quinoline rings, were synthesized with methylene bases V and VIII.



It is interesting to compare the color of the dyes obtained (particularly III) with that of dyes X-XII, which have similar structures ( $\lambda_{max}$  653 [1, 2], 755 [1, 2], and 554 nm [3], respectively) and do not contain an isoindolenine ring in the chromophore:

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Symmetrical locking of the carbon atoms in the 9- and 11-positions through the o-phenylene group results in a large bathochromic shift of the absorption band [2]: the absorption maxima of dyes XI and III are shifted to the longer-wave region by 102 and 69 nm, respectively, as compared with the absorption maxima of dyes X and XII. In agreement with the Dewar-Knott rule [4, 5], replacement of the carbon atom in the 10-position by a nitrogen atom increases the color in dye XII by 99 nm as compared with X and by 132 nm in dye III as compared with XI. A comparison of quinoline dye IX with known compounds XIII ( $\lambda_{max}$  708 nm [6]) and XIV ( $\lambda_{max}$  596 nm [3]) leads to the same conclusions as in the case of III. Cyanine dyes with an isoindolenine ring in the chromophore absorb by about 30 nm in the shorter-wave region than the corresponding dicarbocyanines.



The dyes that we obtained change colors in the presence of acids as a consequence of protonation of the nitrogen atom of the isoindolenine ring. For example, pyridine dye VI forms compound XV [ $\lambda_{max}$  348 nm (log  $\epsilon$  4.36) and 461 nm (log  $\epsilon$  4.54)] which contains two chromophoric conjugation chains.



The presence of two identical conjugated chromophores in the dye molecule results in the appearance of two absorption bands, one of which is shifted to the shorter-wave region, the other of which is shifted to the longer-wave region as compared with the absorption band of the "parent" dye with one similar chromophore [7]. A comparison of the electronic spectra of dye XV with the absorption spectrum of XVI [ $\lambda_{max}$  406 nm (log  $\epsilon$  4.50) [8]], which can be taken as the "parent" dye, indicates that in this case the two absorption bands of dye XV can be considered to be the result of splitting of the absorption band of "parent" dye XVI. Similarly, quinoline dye XVII has two absorption bands [ $\lambda_{max}$  400 nm (log  $\epsilon$  4.26) and 525 nm (log  $\epsilon$  4.50)] which are shifted to the short-wave and long-wave regions as compared with the band of "parent" dye XVIII [ $\lambda_{max}$  448 nm (log  $\epsilon$  4.49) [9]].



Dyes with the XX structure are obtained by the condensation of II with N-substituted rhodanines (XIX).



Solvent	Dielectric constant [10]	$\lambda_{max}$ , nm			
		III	VI	IX	xx
Chloroform Pyridine Ethanol Dimethylformamide Nitromethane Water	4,81 12,3 24,2 37,65 38,6 80,4	633 623 627 621 621	623 626 617 618 613 577	687 689 676 681 675 610	570 569 561 559 

TABLE 1. Absorption Maxima of Dyes in Various Solvents

TABLE 2. Absorption Maxima of Dyes VI and IX in Pyridine-Water Mixtures

Deviding and the first of	Dye VI		Dye IX	
Pyridine concentration, %	λ <sub>max</sub>	lg e	λ <sub>max</sub>	lg e
100 90 70 50 30 10 0	626 622 615 610 604 596 577	4,92 4,90 4,84 4,80 4,78 4,78 4,76	689 685 680 676 673 665 610	4,90 4,89 4,87 4,85 4,83 4,72

The action of alkali on XX markedly deepens the color as a result of the formation of oxanine dyes XXI (in dimethylformamide  $\lambda_{max}$  640, 641, and 643 nm for  $R = CH_3$ ,  $C_2H_5$ , and  $C_6H_5$ , respectively):



All of the dyes that we obtained with an isoindolenine ring in the chromophore change color somewhat as a function of the solvent (see Table 1). In protic solvents (ethanol, for example), the absorption maxima are shifted to the short-wave portion of the spectrum as compared with the absorption in solvents of close polarity. This is apparently explained by the formation of a hydrogen bond between the hydroxyl group of the solvent and the nitrogen atom of the isoindolenine ring, which should increase the color. The absorption maxima of dyes VI and IX in pyridine -water mixtures, taken in various ratios, are presented in Table 2. It is seen from this table that the absorption maxima are gradually shifted to the short-wave part of the spectrum and the absorption intensity decreases when the water concentration is increased. A particularly pronounced shift is observed on passing to pure water; this may be associated with the formation of dimer molecules [11]. However, we could not detect the dimerization of dye VI in water: the Lambert-Beer law was observed. The remaining dyes are only slightly soluble in water, and this hinders a study of their spectra.

Rhodanine dye XX ( $R = CH_3$ ) is alkylated at both sulfur atoms on heating with dimethyl sulfate to give XXII, which is hydrolyzed in 95% alcohol to form dye XXIII.



Dye XXIII and the oxanine dye from it (XXIV) ( $\lambda_{max}$  587 nm) are more highly colored than rhodanine analogs XX.

## EXPERIMENTAL

 $\frac{2-[3-(3-\text{Methyl}-2-\text{benzothiazolinylidene})\text{methyl}-1-\text{isoindolinylidene}]\text{methyl}-3-\text{methylbenzothiazolium}}{\text{Perchlorate (III, X = ClO_4)}$ . A total of 0.55 g (0.0023 mole) of 1,1,3-trichloroisoindolenine (II) [12] and 0.5 g of triethylamine were added to a solution of 1.38 g (0.005 mole) of 2-methylbenzothiazole methylmethosulfate in 10 ml of dimethylformamide. The mixture was heated at 100° for 1 h and then diluted with water. The precipitated dye was filtered and converted to the perchlorate. Two recrystallizations from nitromethane yielded 0.1 g of dye with mp > 300°,  $\lambda_{\text{max}}$  (in alcohol) 575 nm (log  $\varepsilon$  4.51) and 623 nm (log  $\varepsilon$  4.67); in the presence of acid, 505 nm (log  $\varepsilon$  4.48) and 535 nm (log  $\varepsilon$  4.45). Found %: S 11.9; 11.9.  $C_{26}H_{20}CIN_3O_4S_2$ . Calculated %: S 11.9.

 $\frac{2-[3-(1-\text{Ethyl-1},2-\text{dihydro-2-pyridinylidenyl)methyl-1-isoindolinylidenyl]methyl-1-ethylpyridinium}{10\text{dide}\ (VI, X = I).} A 20\% solution of NaOH was added to an aqueous solution of 1 g (0.004 mole) of 2-methyl-pyridine ethiodide, and methylene base V was extracted with benzene. Compound II [0.45 g (0.002 mole)] and 0.8 ml of triethylamine were added to the dried (with solid potassium hydroxide) benzene extract. After 30 min, the precipitated dye was filtered, converted to the iodide, and crystallized from nitromethane to give 0.64 g of blue prisms with mp 248° (decomp.). <math>\lambda_{max}$  (in ethanol) 617 nm (log 4.87); with acid, 348 nm (log 4.36) and 461 nm (log 4.54. Found %: I 26.7, 26.7; N 8.6, 8.6.  $C_{24}H_{24}IN_3$ . Calculated %: I 26.3; N 8.6.

 $\frac{2-[3-(1-Ethyl-1,2-dihydro-2-quinolinylidenyl)methyl-1-isoindolinylidenyl]methyl-1-ethylquinolinium}{Iodide (IX, X = I). A total of 0.7 g of this compound with mp 270° (decomp.) was similarly obtained from 2 g (0.006 mole) of quinaldine ethyltosylate (VII). <math>\lambda_{max}$  (in ethanol) 624 nm (log  $\epsilon$  4.45) and 676 nm (log  $\epsilon$  4.88); with acid, 400 nm (log  $\epsilon$  4.26) and 525 nm (log  $\epsilon$  4.50). Found %: I 21.8, 21.9; N 7.2, 7.2.  $C_{32}H_{28}IN_3$ . Calculated %: I 21.8; N 7.2.

 $\frac{5-[3-(3-\text{Methyl}-4-\text{hydroxy}-2-\text{thiazoline}-5-\text{thionyl})-1-\text{isoindolinylidenyl}]-3-\text{methylrhodanine}}{(XX, R = CH_3)}$ . Triethylamine (1.8 ml) was added to a solution of 1 g (0.007 mole) of 3-methylrhodanine and 0.75 g (0.0035 mole) of II in 5 ml of dimethylformamide, and the mixture was held at room temperature for 30 min. The dye was precipitated by dilution with water, filtered, and washed with hot alcohol and ether to give 0.6 g of product with mp > 300°.  $\lambda_{\text{max}}$  (in dimethylformamide) 562 nm; with alkali, 640 nm (log  $\varepsilon$  5.00). Found %: N 10.4, 10.3. C<sub>16</sub>H<sub>11</sub>N<sub>3</sub>O<sub>2</sub>S<sub>4</sub>. Calculated %: N 10.4.

5-[3-(3-Ethyl-4-hydroxy-2-thiazoline-5-thionyl)-1-isoindolinylidenyl]-3-ethylrhodanine (XX,  $R = C_2H_5$ ). A total of 0.7 g of this compound with mp > 300° (reprecipitated by alcohol from chloroform) was similarly obtained from 1 g of N-ethylrhodanine.  $\lambda_{\text{max}}$  (in dimethylformamide) 565 nm; in the presence of alkali, 641 nm. Found %: N 9.8, 9.8.  $C_{18}H_{15}N_3O_2S_4$ . Calculated %: N 9.7.

 $\frac{5-[3-(3-\text{Phenyl}-4-\text{hydroxy}-2-\text{thiazoline}-5-\text{thionyl})-1-\text{isoindolinylidenyl}]-3-\text{phenylrhodanine} (XX, R = C_6H_5).$  This was similarly obtained and had mp > 300° (reprecipitation by alcohol from chloroform).  $\lambda_{\text{max}}$  (in dimethylformamide) 565 nm. Found %: N 8.2, 8.2. C<sub>28</sub>H<sub>15</sub>N<sub>3</sub>O<sub>2</sub>S<sub>4</sub>. Calculated %: N 7.9.

 $\frac{5-[3-(3-\text{Methyl}-4-\text{hydroxy}-5-\text{thiazolin}-5-\text{onyl})-1-\text{isoindolinylidenyl}]-3-\text{methylthiazolidine}-2,4-\text{dione}}{(XXIII)}$ . A total of 0.2 g of dye XX (R = CH<sub>3</sub>) was heated at 100° for 2 h with a large excess of dimethyl sulfate and then washed with ether. The reaction product (XXII) was dissolved in 95% alcohol by heating. After some time, dye XXIII precipitated from the solution and was purified by reprecipitation from chloroform with alcohol to give 0.1 g of a product with mp > 300°.  $\lambda_{\max}$  (in dimethylformamide) 493 nm; in the presence of alkali, 587 nm. Found %: N 11.0, 11.2.  $C_{16}H_{11}N_{3}O_{4}S_{2}$ . Calculated %: N 11.3.

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