CYANINE DYES BASED ON VINYL DERIVATIVES OF PYRIDINE AND QUINOLINE

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Monomethylidynecyanine dyes containing vinyl groups were obtained by the reaction of the alkiodides of 2-methyl-5-vinylpyridine, 2-vinylquinoline, and 4-methyl-2-vinylquinoline with the appropriate alkiodides of quinoline derivatives.

There is no information in the literature concerning cyanine dyes containing unsubstituted vinyl groups. It is known that the cyanine condensation of alkylhalides of quinoline derivatives proceeds at 100°C [1, 2]. The reaction time increases sharply when the temperature is lowered [2, 3]. When a vinyl group is present in the starting compounds, the rate of the cyanine condensation increases considerably, and the reaction at room temperature is complete in 10-40 min and gives the corresponding dyes (see Table 1). The ease of the reaction is a consequence of the formation of a more stable carbanion that is stabilized by the electrophilic vinyl group (S_N2 mechanism). It should be noted that the alkylhalides of pyridine and quinoline derivatives that do not contain vinyl groups do not undergo the cyanine condensation under the conditions used to synthesize the dyes presented in Table 1.

In a study of the electronic absorption spectra of the synthesized dyes it was noted that different bathochromic shifts of the absorption maxima were observed as a function of the position of the vinyl group. A larger bathochromic shift is observed for dyes of the I type than for dyes of the II and III types. The difference in the shifts of the absorption maxima can be explained by conjugation of the vinyl group with the unshared pair of electrons of the basic nitrogen in dyes I, which is impossible in dyes II and III.

The presence of a vinyl group in the dyes enabled us to work out a method for dyeing polyacrylonitrile fibers [4, 5].

TABLE 1. Cyanine Dyes Containing Vinyl Groups*

Dye	Empirical formula	Found, %				Calc., %				λ_{max}, nm	lg ε	λ_{max},† nm	$\Delta\lambda$, nm
		C	H	I	N	C	H	I	N				
Ia	$C_{21}H_{23}IN_2$	58,2	5,3	29,8	6,6	58,5	5,4	29,5	6,5	568	4,9	513	53
Ib	$C_{21}H_{23}IN_2O$	56,2	5,1	28,9		56,6	5,2	28,5		587	5,3	513	74
Ic	$C_{22}H_{23}IN_2$	59,2	5,2	29,3	6,4	59,6	5,2	28,9	6,3	590	5,7	513	77
IIa	$C_{24}H_{23}IN_2$	61,4	4,9	27,6	6,0	61,8	4,9	27,2	6,0	610	15,3	595	15
IIb	$C_{24}H_{23}IN_2O$	59,4	4,7	26,9		59,7	4,8	26,4		632	17,3	595	37
IIc	$C_{25}H_{25}IN_2O$	60,1	5,1	26,1		60,5	5,0	25,6		634	16,6	595	39
IIIa	$C_{24}H_{23}IN_2$	61,3	4,9	27,7	6,0	61,8	4,9	27,2	6,0	567	11,8	560	7
IIIb	$C_{25}H_{25}IN_2$	62,1	5,15	26,8	5,9	62,5	5,2	26,4	5,8	570	12,3	560	10

*All of the compounds melted with decomposition.

†The absorption maxima of the corresponding dyes without vinyl groups.

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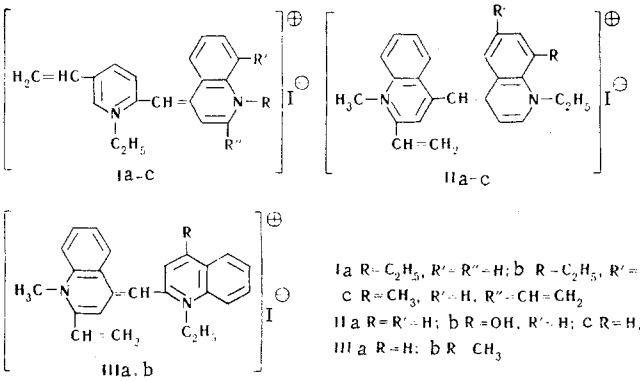

Ia R = C_2H_5, R′ = R″ = H; b R = C_2H_5, R′ = OH, R″ = H; c R = CH_3, R′ = H, R″ = CH = CH_2

IIa R = R′ = H; b R = OH, R′ = H; c R = H, R′ = OCH_3

IIIa R = H; b R = CH_3

EXPERIMENTAL

1,1′-Diethyl-5-vinyl-2,4′-pyridoquinocyanine Iodide (Ia). A solution of 0.56 g (0.01 mole) of potassium hydroxide in 1 ml of methanol was added at 18-20° to a mixture of 2.75 g (0.01 mole) of 2-methyl-5-vinylpyridine ethiodide (IV) and 2.85 g (0.01 mole) of quinoline ethiodide in 40 ml of methanol. After 0.5 h the resulting precipitate was removed by filtration and recrystallized from acetic anhydride to give 1.29 g (30%) of red needles.

1,1′-Diethyl-5-vinyl-8′-hydroxy-2,4′-pyridoquinocyanine Iodide (Ib). This compound was similarly obtained in 65% yield as bright-red needles (from isopropyl alcohol) from IV and 8-hydroxyquinoline ethiodide.

1-Ethyl-1′-methyl-5,2′-divinyl-2,4′-pyridoquinocyanide Iodide (Ic). A solution of 0.56 g (0.01 mole) of potassium hydroxide in 1 ml of methanol was added at 18-20° to a mixture of 2.75 g (0.01 mole) of IV and 2.97 g (0.01 mole) of 2-vinylquinoline methiodide in 50 ml of methanol. After 10 min, the resulting precipitate was removed by filtration. The air-dried precipitate was dissolved in methanol, and the solution was added to a saturated potassium iodide solution. If the dye did not precipitate, a drop of hydriodic acid was added. The resulting elongated plates of the dye were removed by filtration and air-dried at room temperature to give 3.73 g (89%) of product.

1-Methyl-1′-ethyl-2 vinyl-4,4′-quinocyanine Iodide (IIa). A solution of 0.56 g (0.01 mole) of potassium hydroxide in 1 ml of methanol was added at 18-20° to a mixture of 3.11 g (0.01 mole) of 4-methyl-2-vinylquinoline methiodide (V) and 2.85 g (0.01 mole) of quinoline ethiodide in 50 ml of methanol. After 30-40 min, the resulting precipitate was removed by filtration, washed with warm acetone, water, and a small amount of alcohol, and acidified with hydriodic acid to give 3.17 g (68%) of dye IIa. Dye IIa was also obtained in 75% yield via a similar method from 2-vinylquinoline methiodide (VI) and lepidine ethiodide.

1-Methyl-1′-ethyl-2-vinyl-8′-hydroxy-4,4′-quinocyanine Iodide (IIb). This dye was obtained in 89% yield via the method described for IIa from V and 8-hydroxyquinoline ethiodide.

1-Methyl-1′-ethyl-2-vinyl-6′-methoxy-4,4′-quinocyanine Iodide (IIc). This dye was similarly obtained in 80% yield from VI and 6-methoxylepidine ethiodide.

1-Methyl-1′-ethyl-2-vinyl-4,2′-quinocyanine Iodide (IIIa). This dye was similarly obtained in 74% yield from VI and quinaldine ethiodide.

1,4′-Dimethyl-1′-ethyl-2-vinyl-4,2′-quinocyanine Iodide (IIIb). This dye was similarly obtained in 77% yield from VI and 2,4-dimethylquinoline ethiodide.

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