POLYMETHINE DYES, DERIVATIVES OF IMIDAZOPYRIDINE

I. Certain Dyes Which Are Derivatives of 1-Methyl-1H-Imidazo[4, 5-c]Pyridine

A. V. Kazymov, L. P. Shchelkina, L. V. Ivanova, N. V. Monich, and A. F. Vompe

Khimiya Geterotsiklicheskikh Soedinenii, Vol. 6, No. 2, pp. 228–233, 1970

UDC 668.8: 547.785.5'821

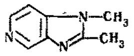
Certain new polymethine dyes of the cyanine, merocyanine, and merocyaninocyanine series containing residues of the quaternary salt of 1-methyl-1H-imidazo[4, 5-c]pyridine have been synthesized. A study was made of the coloration of synthesized dyes. Replacement of the benzimidazole residue in the cyanine dyes by the residue of the quaternary salt of 1-methyl-1H-imidazo[4, 5-c]pyridine leads to the intensification of the color of the dyes.

Recently, in a number of patents and works, it has been mentioned that imidacarbo- and merocyanines, containing electronegative substitutes in the heterocyclic residues have a marked sensitizing action on photographic silver halide emulsions [1].

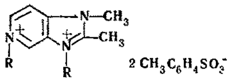
It was of interest to study the properties of analogs of these dyes containing the imidazopyridine residue, in which the cyclic nitrogen atom of the pyridine ring may be regarded as an electronegative substitute. In this regard dyes were synthesized which contained residues of 1-methyl-1H-imidazo[4, 5-c]pyridine. To the present time these dyes have not been described in the literature.

1, 2-Dimethyl-1H-imidazo[4, 5-c]pyridine (I) was obtained by heating 3-amino-4-methylaminopyridine (II) with acetic aldehyde in the presence of copper acetate [2] or with acetic anhydride [3]. Compound II was synthesized from 3-nitro-4-methoxypyridine [4] via 3-nitro-4-methylamino pyridine [5]. An attempt was made to synthesize 3-nitro-4-amino and -4-alkylaminopyridines by the interaction of 3-nitro-4-oxypyridine [6] with ammonia or alkylmaines. It was found that by this means 3-nitro-4-aminopyridine may readily be obtained.

During the interaction between the base of compound I and ethyl iodide, the iodoethylate (III) was obtained which did not participate in the condensation reaction with orthoformic ethyl ether (in a medium ofnitrobenzene). Apparently in this case alkylation proceeded at the nitrogen atom of the pyridine ring. Under more severe conditions on heating the base of compound I with the alkyl esters of p-toluene-sulfonic acid at 120° C double quaternary salts (IVc) were obtained.



I

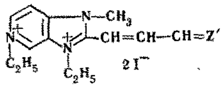


IV a–c

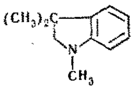
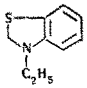
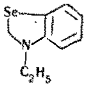
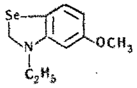
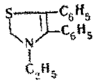
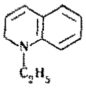
a R=CH_3; b R=C_2H_5; c R=p-C_3H_7

It was found that the compounds IV possess an extremely active methyl group. According to their reaction capacity they exceeded the quaternary salts of 1-alkyl-2-methylbenzimidazoles. Thus for example it was possible to use the double quaternary salt IVb for the synthesis of the corresponding dicarbocyanine (V) on condensation of it with 1, 1, 3, 3-tetraethoxypropane [7], whereas the quaternary salts of 1-alkyl-2-methylbenzimidazoles do not enter such a condensation. In addition, on interaction of compound IVb with orthoformic ethyl ether in a medium of nitrobenzene, a symmetrial carbocyanine (VI) was obtained. One should note that this dye is formed under more mild conditions than 1, 1', 3, 3'-tetraalkylsubstituted imidacarbocyanes [8].

Table 1



VII a–e

Compound	Z′	Temperature and duration of the reaction °C	External appearance (from ethanol)	Mp, °C	Empirical formula	N, %		λ_{max}, nm			Hypsochromic displacement, nm	Yield, %
						Found	Calculated	Found (in ethanol)	Calculated	Symmetrical carbocyanine		
VIIa*		140 (4)	Dark red needles	178—180	$C_{25}H_{32}Cl_2N_4O_8$	9.3; 9.4	9.5	530	536.5	548	6.5	13.3
VIIb		130 (4)	Greenish needles	267—270	$C_{23}H_{28}I_2N_4S$	8.8; 8.9	8.7	540	541.5	558	1.5	25.8
VIIc		140 (2)	Dark-violet needles	255—256	$C_{23}H_{28}I_2N_4Se$	7.9 8.2	8.1	548	548.5	572	0.5	27
VIId		140 (5)	Red-brown needles	260—262	$C_{24}H_{30}I_2N_4OSe$	8.4 8.5	8.4	560	—	—	—	37.5
VIIe		140 (2)	Dark-violet needles	261—262	$C_{31}H_{34}I_2N_4S$	7.3 7.4	7.5	555	—	—	—	18.8
VIIf		140 (3)	Dark-violet needles	270—271	$C_{25}H_{30}I_2N_4$	8.7	8.8	562	565	605	3	46.7

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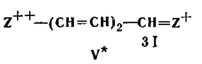
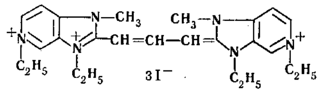
*Diperchlorate.



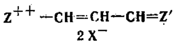
$Z^{++}—(CH=CH)_2—CH=Z^+$ $3I$

V*



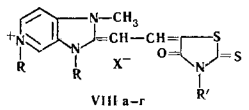
VI

In the subsequent condensation of compound IVb with quaternary salts of 2-(ω-acetanilinovinyl)-or-2-(methylthiovinyl)substituted heterocyclic bases in pyridine, a number of assymmetrical carbocyanine dyes (VIIa–VIIf, table 1) was synthesized.



$Z^{++}—CH=CH—CH=Z'$ $2X^-$

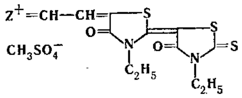
VII a–e



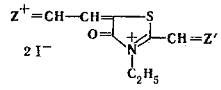
VIII a–r

a $R=R'=C_2H_5$, $X=I$; b $R=C_2H_5$, $R'=CH_2CH=CH_2$, $X=CH_3C_6H_4SO_3$; c $R=CH_3$, $R'=C_2H_5$, $X=CH_3C_6H_4SO_3$; d $R=p\text{-}C_3H_7$, $R'=C_2H_5$, $X=I$

By the interaction of compounds IVa–IVc with 5-acetanilinomethylene-3-alkylrhodanines in pyridine, a number of dimethinemerocyanines (VIIIa–VIIId, table 2) were obtained. The merocyanine of compound VIIIa is readily alkylated during the action of dimethyl sulfate at the thionyl sulfur, with the formation of the quaternary salt (IX). The latter condenses with the formation of dimerocyanine (X).



X



XI a–c

During the interaction of compound IX with the quaternary salts of different nitrogeneous heterocyclic bases containing an active methyl group, merocyanines (XIa–XIc, table 3) were synthesized.

Table 2. Dimethinemerocyanines

Compound	Mp, °C	λ_{max}, nm (in ethanol)	Empirical formula	N, %		Yield, %
				Found	Calculated	
VIIIa	265—267	520	$C_{18}H_{23}JN_4OS_2$	11.4	11.2	61.5
VIIIb	256—257	520	$C_{26}H_{30}N_4O_4S_3$	9.3	10.0	55.0
VIIIc	286—287	520	$C_{23}H_{26}N_4O_4S_3$	10.6	10.8	58.8
VIIId	224—225	525	$C_{20}H_{27}JN_4OS_2$	10.3	10.6	36

The pyridine rings of all the above-mentioned dyes were found in the onium state. Because of this condition the dyes are readily soluble in alcohol and water. All the dyes studied are characterized by their marked capacity to be adsorbed by aluminum oxide.

A study was made of the absorption spectra of alcoholic solutions of the synthesized dyes. The maximum of the absorption of the symmetrical carbocyanine dye VI (525 nm) is displaced in comparison with the absorption maximum of 1, 1'-dimethyl-3, 3'-diethylimidacarbocyanine iodide [9] in the wavelength region of the spectrum by 35 nm. The hypsochromic displacement of the absorption maximum of a number of asymmetrical carbocyanines VII, containing residues of 3, 3-dimethylindolenine, benzothiazole, benzeselenazole, quinoline, in comparison with the calculated values are not more than 6.5 nm (Table 1, [10]). It follows from these data that the basicity of the residue of the quaternary salt of imidazo[4, 5-c]pyridine is apparently close to the basicity of the benzothiazole residue.

The absorption maximum of the dimethinemerocyanine of compound VIIIa is displaced in comparison with that observed with the corresponding imidadimethinemerocyanine (XII) [9] by 9 nm. The hypsochromic displacement of the absorption maximum for compound VIIIa, arising from the corresponding symmetrical dyes, comprises 12.5 nm. The analogous hypsochromic displacement, found with imidadimethinemerocyanone XII, is only 4 nm [9].

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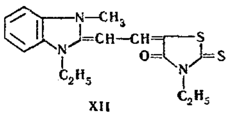
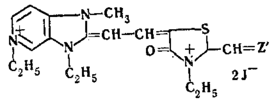
*Here and subsequently Z^+ and Z^{++} denote respectively the single and double charged residue of 1-methyl-1H-3, 5-diethylimidazo[4, 5-c]pyridinium.



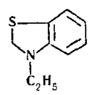
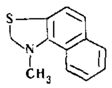
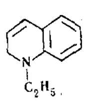
XII

From these observations it follows that the residue of the quaternary salt of imidazopyridine (Z^+) in the dyes examined, as one would expect, possesses less basicity than the benzimidazole residues in the corresponding dyes.

Table 3



XI a–c

Compound	Z′	External appearance (from ethanol)	Mp, °C	λ_{max}, nm (in ethanol)	Empirical formula	N, %		Yield, %
						Found	Calculated	
XIa		Greyish-green needles	270–271	585	$C_{28}H_{33}I_2N_5OS_2$	8.8	9.0	37.5
XIb		Violet needles	275–276	590	$C_{31}H_{33}I_2N_5OS_2$	8.8	8.6	10
XIc		Blue needles	264–265	604	$C_{30}H_{35}I_2N_5OS$	8.9	9.1	5.2

The synthesized dyes are sensitizers of silver halide emulsions [11]. Their photographical properties will be examined later.

EXPERIMENTAL*

3-Nitro-4-aminopyridine. A mixture of 0.7 g (0.05 mole) of 3-nitro-4-oxypyridine [6] and 5 ml of a 25% aqueous solution of ammonia was heated in a sealed tube for 3.5 hr at 175° C. Bright yellow crystals were removed by filtration and washed in water. Yield, 0.49 g (70.0%); mp 201–203° C [12].

3-Amino-4-methylaminopyridine. (II). A 3.52 g (0.023 mole) quantity of 3-nitro-4-methylaminopyridine was added to a hot solution (80° C) of 11.05 g (0.046 mole) of sodium sulfide in 45 ml water. The mixture was heated for 45 min at 100° C. The solution was evaporated approximately to half volume, and the precipitate was removed by filtration and washed with water. Yield, 2.32 g (82%). Yellowish crystals, mp 170–172° C [2].

1, 2-Dimethyl-1H-imidazo[4, 5-c]pyridine (I). A mixture of 1.48 g (0.012 mole of compound II and 10 ml acetic anhydride was heated for 3 hr at 140° C. The excess of acetic anhydride was distilled off under vacuum, the precipitate was dissolved in water, the solution was made alkaline with potash, and the base was extracted with chloroform. Yield, 1.27 g (86.3%). Colorless needles, mp 173–175° C [2] (from benzene).

Ditosylate of 1, 2-dimethyl-3, 5-diethylimidazo[4, 5-c]pyridine (VIb). A 0.49 g (3.3 mM) quantity of 1, 2-dimethyl-1H-imidazo[4, 5-]pyridine and 1.97 g (9.9 mM) of the ethyl ester of p-toluene-sulfonic acid was heated for 15 hrs at 120° C. After washing with dry benzene and grinding with a mixture of benzene and acetone the resin-like mass crystallizes. Yield, 1.38 g (78%). Colorless prisms (from a mixture of ethanol and benzene, 1 : 10), mp 178–180° C Found, %: N 7.4. Calculated for: $C_{26}H_{33}N_3O_6S_2$, %: N 7.7.

Compounds IVa and IVc which were used in subsequent reactions without additional purification were obtained

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*The authors wish to express their thanks to E. M. Perel', who participated in the experimental part of this work.

under similar conditions.

Iodoethylate of 1, 2-dimethyl-1H-imidazo[4, 5-c]pyridine (III). A 1.47 g (0.01 mole) quantity of compound I and 4 ml of ethyl iodide were heated for 5 hrs. After washing with dry acetone 1.96 g of compound III (64.7%) was obtained. Colorless crystals, mp 200° C (from ethanol). Found, %: N 13.7, 13.8. Calculated for $C_{10}H_{14}IN_3$, %: N 13.9.

Bis(1-methyl-3, 5-diethylimidazo[4, 5-c]pyridinium-2, 2')trimethinecyanintriiodide (VI). A mixture of 0.17 g (0.35 mM) of compound IVb, 0.15 g (1 mM) of orthoformic ethyl ether, and 2 ml of nitrobenzene was heated for 4 hrs at 130° C. The dye was precipitated with ether and isolated in the form of the iodide. Yield, 0.05 g (41.6%). Red needles, mp 263–264° C (from ethanol), λ_{max} 525 nm (in ethanol). Found, %: N10.5.* Calculated for $C_{25}H_{35}I_3N_6$, %: N 10.5.

1-Methyl-3, 5, 3'-triethyl(imidazo[4, 5-c]pyridinium-2)thiacarbocyanine diiodide (VIIb, Table 1). A mixture of 0.4 g (0.8 mM) of compound IVb, 0.28 g (0.8 mM) of the methylsulfate of 3-ethyl-2-(β-methylthiovinyl) benzthiazolium, 12 ml of dry pyridine, and 0.1 ml of triethylamine was heated for 4 hr at 37° C. The dye was precipitated with ether, subjected to chromatography on aluminum oxide (solution in chloroform), and converted into the iodide.

In a similar manner the asymmetrical carbocyanines of VIIa, c–f (Table 1) were obtained by condensation of compound IVb, respectively, with iodomethylate of 2-(β-acetanilinovinyl)-3, 3-dimethylindolenine, with the methyl sulfate of 3-ethyl-2-(β-methylthiovinyl)benzoselenazolium, with the iodide of 3-ethyl-2-(β-anilinovinyl)-4, 5-diphenylthiazolium, and with the toxylate of 3-ethyl-2-(β-anilinovinyl)quinolinium. On production of compounds VIIe and VIIf apart from triethylamine acetic anhydride was added (approximately 0.3 ml per 0.4 g of IVb).

Dimethinemerocyanines (VIIIa–VIIId, Table 2). A mixture of 0.3 mM of the corresponding IV compound., 0.3 mM of 3-alkyl-5-acetanilinomethylenerhodanine, 4 ml of dry pyridine, and 0.1 ml of triethylamine was heated for 4 hrs at 140° C. The dye was precipitated with ether (VIIIa, d were converted into the iodide). The compounds crystallized from ethanol in the form of red (VIIa, b) or brown (VIIIc, d) needles.

Dimethinemerocyaninocyanines (XIa–c, Table 3). A 0.06 g (0.1 mM) quantity of compound VIIIa ($X = CH_3C_6H_4SO_3$) and 0.02 g (0.15 mM) of dimethyl sulfate were heated for 30 min at 135° C. A 0.1 mM quantity of the quaternary salt of the corresponding heterocyclic base and 3 ml of dry pyridine were added, and the mixture was heated for 4 hrs at 135° C (for XIa, the mixture was heated for 3 hrs at 135° C). The dye was precipitated with ether and converted into the iodide. The compound was crystallized from ethanol.

Dimerocyanine (X). A 0.14 g (0.25 mM) quantity of the dimethinemerocyanine of compound VIIIa and 0.2 g dimethyl sulfate were heated for 30 min at 135° C. The dark-red mass was washed with benzene, dissolved in 2 ml dry pyridine, and 0.07 g (0.3 mM) of 3-ethylrhodanine was added and the mixture was heated for 4 hrs at 140° C. The dye was isolated with ether and washed with alcohol. Yield, 0.06 g (35.3%). Brown crystals (from ethanol), mp 284–286° C; λ_{max}, 565 nm (in ethanol). Found, %: N 11.3; 11.1. Calculated for $C_{24}H_{31}N_5O_6S_4$, %: N 11.4.

Bis(1-methyl-3, 5-diethylimidazo 4, 5-c pyridinium-2, 2')dicarbocyanintriiodide (V). A mixture of 0.3 g (0.54 nM) of compound IVb, 0.07 ml (0.27 mM) 1, 1, 3, 3-tetraethoxypropane, 11 ml of dry pyridine, and 0.2 ml triethylamine was heated for 4 hrs at 120° C. The dye was precipitated with ether, and isolated in the form of the iodide. Yield, 0.07 g (31.4%); mp 240–242° C; after washing with boiling ethanol it does not change. Green crystals; λ_{max} 635 nm (in ethanol). Found, %: N 10.1. Calculated for $C_{27}H_{37}I_3N_6$, %: N 10.2.

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*For the analysis in all cases the dyes were dried over phosphorus pentoxide at 100° C.

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4 March 1968

All-Union State Scientific-Research and Planning Institute
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