PYRYLOCYANINES

VI.* CONVERSION OF 4-PYRYLOCYANINES TO 4-PYRIDOCYANINES

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Depending on the reaction conditions, in the reaction of symmetrical 2,6-diphenyl-4-pyrylomonomethine-, carbo-, and dicarbocyanines with methylamine the oxygen atoms in one or both pyrylium residues are replaced to give both unsymmetrical pyrylopyrido- and symmetrical pyridocyanines. The deviations for the synthesized dyes increase as the lengths of the polymethine chromophore increases.

In contrast to the data for pyrylium salts [2], little is known about the reactions of pyrylocyanines with nucleophilic agents. The information for salt-form pyrylocyanines is limited to the reaction of pyrylomonomethinecyanines with sodium sulfide [3] and methylamine [4], and the transformations of dyes containing only 2,6-dimethyl-substituted pyrylium rings have been described in the latter case. In the pyrylotrimethinecyanine series only the reaction of (9-xanthylo) (4,6-diphenyl-2-pyrylo)trimethinecyanine [5], in which the pyrylium residue retains high activity, with methylamine is known.

In the present research we investigated the reaction of a number of 2,6-disubstituted pyrylomono-, tri-, and pentamethinecyanines with methylamine. The positive charge in the pyrylocyanine is diffused over the entire mesomeric cation, and they therefore should have activity with respect to nucleophilic agents as compared with pyrylium salts. When the oxygen atom is replaced by a $N-CH_3$ group in one of the pyrylium rings, the activity of the other pyrylium rings should be reduced because of migration of the positive charge to the residue of the more "basic" nitrogen heteroring. Up until now the oxygen atom in only one of the pyrylium rings could be replaced, for example, in the reaction of unsymmetrical (2,6-diphenyl-4-pyrylo)-(2,6-dimethyl-4-pyrylo)monomethinecyanine (I) with methylamine in methanol [4]. From a comparison of the PMR spectrum of pyrylopyridomonomethinecyanine II in trifluoroacetic acid, in which the dye forms salt III, with the PMR spectra of 2,4,6-trimethyl- and 2,4-diphenyl-4-methyl-substituted pyrylium [6] and N-methylpyridinium [7] salts we showed that the oxygen atom in the pyrylium residue containing methyl groups in monomethinecyanine I is replaced first to give II. Even on prolonged heating in methanol the second oxygen atom is not replaced by a methylamino group. However, if the reaction of monomethinecyanine I with methylamine is carried out in an aprotic polar solvent [dimethylformamide (DMF) or dimethyl sulfoxide (DMSO)], the oxygen atom in the second pyrylium residue is also replaced to give pyridomono-, methinecyanine IV. It was found that dyes V-VII, XII-XIV, and XIX (Table 1) on reaction with methylamine can also be initially converted to unsymmetrical pyridocyanines VIII-X, XV-XVII, and XX, and to symmetrical pyridomono-, tri-, and pentamethinecyanines XI, XVIII, and XXI on heating in an aprotic solvent. (See scheme on following page.)

The orders of the carbon–carbon bonds in the chromophores of polymethine dyes constructed from heterocyclic residues that differ sharply in "basicity" differ appreciably. As we have shown in [1], in dyes of this sort the electron transition corresponding to the long-wave absorption band occurs with higher probability with a change in the vibrational quantum number than without a change. This is also confirmed in

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*See [1] for communication V.

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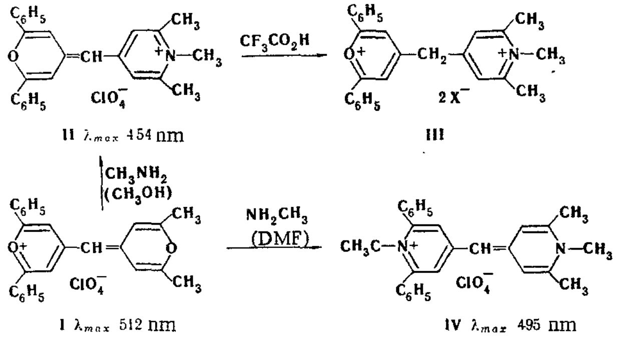

the group of dyes obtained in this study. In fact (Fig. 1), the long-wave band of symmetrical trimethinecyanine XII has the form characteristic for polymethine dyes with a sharp drop into the long-wave region. A similar form of the curve is observed for symmetrical pyridotrimethinecyanine XVIII. On the other hand, the absorption band of unsymmetrical trimethinecyanine XV (in nitromethane) has a very sloping drop into the long-wave region. A maximum, which in nitromethane does not appear distinctly because of the diffuse character of the band, is observed in the absorption spectrum of the latter compound in methylene chloride on the long-wave branch. In the spectra of pyridothiopyrylotrimethinecyanine XIII and pyridopyrylopentamethinecyanine XX in methylene chloride the bands corresponding to the low-energy transition also have shoulders on the long-wave branch, although they are less pronounced than in the case of trimethinecyanine XV; this is associated with the high electronic asymmetry of these dyes. Because of the lower "basicity" of the selenopyran residue in pyridoselenopyrylotrimethinecyanine XVIII, the long-wave maximum is of such low intensity that it does not appear at ordinary temperatures even in methylene chloride.

In order to determine the relative "basicities" of the heterocyclic rings of the polymethine dyes one usually employs the method of calculation of the deviations (D) – the deviations of the absorption maxima of an unsymmetrical dye from the arithmetic mean value of the maxima of two symmetrical dyes [10]. In addition to calculation of the deviations (D) with respect to the maxima, we also determined the deviations (D_M), as in preceding studies [1, 11], from the average position of the absorption bands (M^{-1}). The low deviations observed for monomethinecyanines VI and VII and the extinctions of these dyes (Table 1) confirm the previous conclusion regarding the close "basicities" of the O-, S-, and Se-containing heterocycles under consideration [1]. However, a comparison of the deviations in series of unsymmetrical pyridomono- and pyridotrimethinecyanines VIII-X and XV-XVII confirms the conclusion [1] regarding the change in their "basicities" as a function of the heteroatom in the order O > S > Se. A comparison of the magnitudes of the vinylene shifts and the deviations in the series of unsymmetrical dyes VII, XV, and XX, which contain pyridinium and pyrylium residues, is worthy of special attention, inasmuch as one cannot draw a conclusion regarding the principles of the vinylene shifts for unsymmetrical polymethine dyes from the literature data [12-14]. In contrast to the pyrylo- and pyridocyanines of symmetrical structure, a sharp decrease in the vinylene shift as the length of the polymethine chromophore increases is observed for the unsymmetrical dyes under consideration (the vinylene shift is 78 nm on passing from monomethinecyanine VIII to carbocyanine XV, whereas the shift is 34 nm on passing from XV to dicarbocyanine XX). A clear regularity is also observed in the magnitudes of the deviations. The data presented above show that the deviations (expressed both in wavelengths and in frequencies) of unsymmetrical polymethine dyes constructed from heterocyclic residues that differ sharply with respect to their "basicities" increase as the chromophore becomes longer.

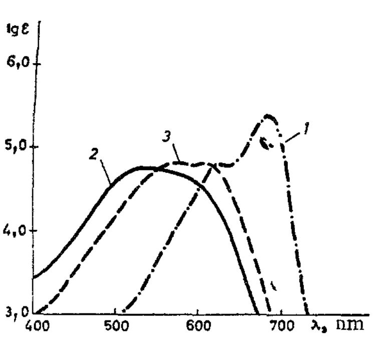

Fig. 1. Absorption spectra: 1) pyrylotrimethinecyanine XII in CH_3NO_2; 2) pyrylopyridotrimethinecyanine XV in CH_3NO_2; 3) XV in CH_2Cl_2.

EXPERIMENTAL METHOD

The electronic absorption spectra were recorded with an SF-4A spectrophotometer. The PMR spectrum of a solution of salt III in 0.1 M CF_3COOH was determined with a Tesla BF487B spectrometer with an operating frequency of 80 MHz at 20° with tetramethylsilane as the internal standard: 8.37 s* (2H), β-H of the pyranylidene residue; 8.30 m (4H), o-H of the phenyl sub-

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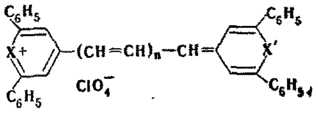
*Abbreviations: s is singlet and m is multiplet.

TABLE 1. Characteristics of the Long-Wave Absorption Bands of Pyrylocyanines V-XXI in Nitromethane



V-XXI

Compound	n	X	X′	λ_{max}, nm	lg ε	M^{-1}, nm	D,† nm (D_ν, cm^{-1})	D_M, nm ($D_{M\nu}$, cm^{-1})
V*	0	O	O	552	5,04	538	—	—
VI	0	O	S	588	5,09	580	2	—
VII	0	O	Se	610	5,11	602	2	—
VIII	0	O	NCH_3	476	4,62	463	56 (2210)	58 (2410)
IX	0	S	NCH_3	505	4,68	493	65	68
X	0	Se	NCH_3	508	4,61	493	84	89
XI	0	NCH_3	NCH_3	512	5,01	504	—	—
XII‡	1	O	O	676	5,39	658	—	—
XIII[1]	1	O	S	715	5,19	—	0,5	—
XIV[1]	1	O	Se	734	5,31	—	0,5	—
XV	1	O	NCH_3	554	4,77	538	103 (2830)	98 (2870)
XVI	1	S	NCH_3	564	4,61	542	132 (3370)	131 (3580)
XVII	1	Se	NCH_3	560	4,68	545	156 (3900)	144 (3840)
XVIII	1	NCH_3	NCH_3	638	—	614	—	—
XIX	2	O	O	798	5,40	757	—	—
XX	2	O	NCH_3	588	4,69	573	185 (4070)	161 (3840)
XXI	2	NCH_3	NCH_3	748	—	711	—	—

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* For the sulfur analog of this dye [8], λ_{max}, log ε, and M^{-1} are 628 nm, 5.10, and 6.17 nm, as compared with 672 nm, 5.13, and 661 nm for the selenium analog [8].

†See [10].

‡The ε value presented in [9] (117,000) is too low.

TABLE 2

Compound	mp (dec.), °C (crystallization solvent)	Empirical formula	Found, %	Calc., %	Yield, %
IV	148 methanol—water, 1 : 1)	$C_{27}H_{27}ClN_2O_4$	C 67,7; H 5,5 Cl 7,4; N 5,4	C 67,7; H 5,6 Cl 7,4; N 5,8	83
VII	265—266 (acetonitrile)	$C_{35}H_{25}ClO_5Se$	Cl 5,5; Se 12,7	Cl 5,5; Se 12,4	60
VIII	272—273 (acetic acid)	$C_{36}H_{28}ClNO_5$	Cl 6,0	Cl 6,0	72
IX	163 (methanol—water, 5:1)	$C_{36}H_{28}ClNO_4S$	Cl 5,8; S 5,4	Cl 5,9; S 5,2	41
X	156 (acetic acid)	$C_{36}H_{28}ClNO_4Se$	Cl 5,4; Se 12,2	Cl 5,4; Se 12,1	83
XI	227 (methanol)	$C_{37}H_{31}ClN_2O_4$	Cl 5,8; N 4,95	Cl 5,9; N 4,6	79
XV	258 (acetic acid)	$C_{38}H_{30}ClNO_5$	Cl 5,9	Cl 5,9	58
XVI	207 (acetic acid)	$C_{38}H_{30}ClNO_4S$	S 5,0	S 5,0	67
XVII	211—212 (acetic acid)	$C_{38}H_{30}ClNO_4Se$	Cl 5,5; Se 11,7	Cl 5,2; Se 11,4	81
XVIII	194—195 (ethanol)	$C_{39}H_{33}ClN_2O_4$	Cl 5,7; N 4,5	Cl 5,6; N 4,4	83
XIX	274 (acetic anhidride)	$C_{39}H_{29}ClO_6$	Cl 5,6	Cl 5,6	82
XX	203—204	$C_{40}H_{32}ClNO_5$	Cl 5,7	Cl 5,5	78
XXI	186—187	$C_{41}H_{35}ClN_2O_4$	Cl 5,5; N 4,3	Cl 5,4; N 4,3	68

stitutents; 7.84 s (2H), β-H of the pyridinium ring; 7.77 m (6H), m, p-H of the phenyl substituents; 4.80 s (2H), methylene group H; 4.25 s (3H), H of the NCH_3 group; 2.92 ppm s (6H), H of the methyl groups in the 2 and 6 positions of the pyridinium residue.

The purity of the preparations was monitored by thin-layer chromatography (TLC). Chromatography was carried out on plates with a fixed layer of Silufol-254 silical gel with elution by nitromethane.

1,2,6-Trimethyl-4-[(1-methyl-2,6-diphenyl-4-pyridylidene)methyl]pyridinium Perchlorate (IV). This compound was obtained by heating a solution of 0.36 g (0.8 mmole) of I in 10 ml of DMF with an excess of a methanol solution of methylamine at 100° for 30 min. The mixture was then cooled and diluted with water, and the precipitated dye was removed by filtration and crystallized. The physical characteristics of this dye and the remaining newly synthesized dyes are presented in Table 2. In the recrystallization of IV and symmetrical pyridocyanines XI, XVIII, and XXI, methylamine was added to the solvent.

2,6-Diphenyl-4-{[2,6-diphenyl-4(1H)-seleno-4-pyranylidene]methyl}pyrylium Perchlorate (VII). A 0.409-g (1 mmole) sample of 2,6-diphenyl-4-methylselenopyrylium perchlorate [15], 0.511 g (1.1 mmole) of 2,6-diphenyl-4-methoxypyrylium o-nitrobenzenesulfonate, and 0.082 g of anhydrous sodium acetate were heated in 10 ml of a mixture (1 : 1) of acetic anhydride and glacial acetic acid at 100° for 30 min. The resulting dye was purified by reprecipitation from acetonitrile by the addition of 20% $HClO_4$ and crystallization.

1-Methyl-2,6-diphenyl-4-{[2,6-diphenyl-4(1H)-4-pyranylidene]methyl}pyridinium Perchlorate (VIII). A 0.232-g (0.4 mmole) sample of pyrylomonomethinecyanine V [9] was heated with excess methylamine in 6 ml of absolute methanol for 30 min, after which the solution was cooled, and the precipitated dye was removed by filtration and crystallized.

Unsymmetrical Pyridomonomethinecyanines IX and X and Symmetrical Pyridomonomethinecyanine XI. These dyes were obtained from monomethinecyanines VI [3], VII, and V, respectively, under the conditions used to obtain dye IV.

1-Methyl-(2,6-diphenyl-4-pyrido)(2,6-diphenyl-4-pyrylo)trimethinecyanine Perchlorate (XV). A 0.24-g (0.4 mmole) sample of XII [16] in 8 ml of DMF was maintained with an excess of a methanol solution of methylamine at room temperature for 30 min. The solution was then diluted with water and treated with a few drops of 20% $HClO_4$. The precipitated dye was removed by filtration.

1-Methyl-(2,6-diphenyl-4-pyrido)(2,6-diphenyl-4-thiopyrylo)trimethinecyanine Perchlorate (XVI). This dye was obtained from XIII [1] as in the preceding experiment.

(1-Methyl-2,6-diphenyl-4-pyrido)(2,6-diphenyl-4-selenopyrylo)trimethinecyanine Perchlorate (XVII). This dye was obtained from XIV [1] and methylamine in DMSO by heating to 50° for 1 h.

Bis(1-methyl-2,6-diphenyl-4-pyrido)trimethinecyanine Perchlorate (XIII). This dye was obtained by heating 0.3 g (0.5 mmole) of XII with an excess of a methanol solution of methylamine in 10 ml of DMSO at 95° for 1.5 h. The dye was isolated as in the case of XV.

Bis(2,6-diphenyl-4-pyrylo)pentamethinecyanine Perchlorate (XIX). A 0.346-g (1 mmole) sample of 2,6-diphenyl-4-methylpyrylium perchlorate, 0.082 g of anhydrous sodium acetate, and 0.129 g (0.5 mmole) of malonic dialdehyde dianil hydrochloride were heated in 5 ml of acetic anhydride–acetic acid (1 : 1) at 110-120° for 30 min. The precipitated dye was removed by filtration.

1-Methyl-2,6-diphenyl-4-pyrido)(2,6-diphenyl-4-pyrylo)pentamethinecyanine Perchlorate (XX). This dye was obtained by maintaining a solution of XIX in nitromethane with excess methylamine at room temperature for 1 h. The dye was precipitated by dilution with alcohol (1 : 1) and the addition of 20% $HClO_4$. The precipitated dye was removed by filtration and washed with water, alcohol, and ether.

Bis(1-methyl-2,6-diphenyl-4-pyrido)pentamethinecyanine Perchlorate (XXI). This dye was obtained by heating dye XIX in DMSO with excess methylamine at 70° for 1 h. The solution was then cooled and diluted with ice water, and 20% $HClO_4$ was added. The precipated dye was removed by filtration and washed with ether.

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