PYRYLOCYANINES.

16.* TETRAPHENYL-SUBSTITUTED (2-PYRYLO)(4-PYRYLO)CYANINES

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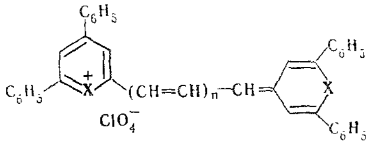
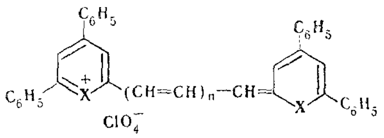
Unsymmetrical tetraphenyl-substituted (2-pyrylo)(4-pyrylo)monomethylidyne-, carbo-, and dicarbocyanines and their thiopyrylium and pyridinium analogs were synthesized. The absorption spectra of these dyes were studied. The spectral characteristics of their long-wave absorption bands have values that are intermediate between the analogous characteristics of the corresponding symmetrical isomers of the α and γ series.

We have previously investigated symmetrical (2-pyrylo)(4-pyrylo)cyanines and their sulfur- and nitrogen-containing analogs Ia,b-IXa,b [2], as well as the corresponding (pyrylo)-(thia)- and (pyrylo)(indo)cyanines, which have markedly expressed electronic asymmetry [3].

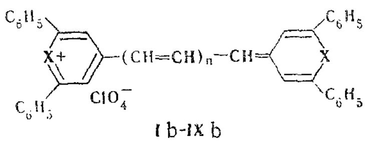
It seemed of interest to compare the spectral properties of asymmetrical (2-pyrylo)-(4-pyrylo)cyanines with structures I-III, as well as their sulfur- and nitrogen-containing analogs IV-IX, with the properties of the isomeric symmetrical Ia,b-IXa,b, in which the heterocyclic residues are connected to the polymethine chain only in the 2 or 4 position.



I–IX



Ia-IXa



Ib-IXb

I—III X=O; IV—VI X=S; VII—IX X=NCH_3; I, IV, VII n=0; II, V, VIII n=1; III, VI, IX n=2.

Pyrylomonomethylidynecyanine I was synthesized by condensation of 2-methyl-4,6-diphenylpyrylium perchlorate (Xa) with 2,6-diphenyl-4H-pyran-4-one as in [4]. We obtained the corresponding trimethylidynecyanine II [5] by two pathways: by reaction of salt Xa with 2,6-diphenyl-4-formylmethylene-4H-pyran (XIII) and by condensation of the corresponding isomeric compounds, viz., the 2,6-diphenyl-4-methylpyrylium salt (XIa) and 4,6-diphenyl-2-formylmethylene-2H-pyran (XIIa). Pyrylodicarbocyanine structure III was previously described in [3]. The thiopyrylocyanines were synthesized in the same way as their oxygen-containing analogs: monomethylidynecyanine IV from 2,6-diphenyl-1-thio-4H-pyran-4-one and thiopyrylium perchlorate Xb, carbocyanine V by reaction of XIb and XIIb, and dicarbocyanine VI by condensation of the same salt XIb with 2-(4-ethoxy-1,3-butadienyl)-4,6-diphenylthiopyrylium perchlorate. Pyridocyanines VII-IX were obtained by treatment of pyrylocyanines I-III

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*See [1] for communication 15.

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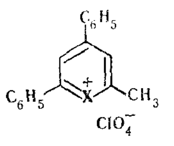
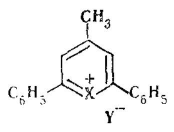
TABLE 1. Characteristics of the Long-Wave Absorption Bands of the Dyes

Dye	λ_{max}, nm	lg ε	M^{-1}, nm	D_M, nm	f	σ	γ_1	γ_2	F
In methylene chloride									
I	565, 603	4,66; 4,81	571,3	−2,4	0,65	1188	1,15	2,1	0,054
II	740	4,99	697,2	5,2	0,97	1056	1,03	1,5	0,045
III	862	5,14	807,6	−0,4	1,26	998	1,24	2,4	0,059
IV	662	4,88	638,4	−19,6	0,64	970	0,91	1,2	0,034
V	780, 820	4,93; 4,96	779,9	1,8	0,91	917	0,97	1,4	0,036
VI	895	5,18	881,5	9,8	1,19	944	1,10	2,5	0,040
VII	532	4,61	510,9	1,9	0,52	1396	1,20	2.9	0,056
VIII	635	5,13	617,5	−1,3	1,02	942	1,31	3,2	0,055
IX	744	5,29	723,0	−4,1	1,21	954	1,49	3,9	0,069
In acetonitrile									
I	595	4,79	565,7	−1,9	0,68	1220	1,09	2,0	0,047
I a	(590) 635	4,66	592,8		0,94	1388	1,19	2,4	0,058
I b	550	5,13	534,9		1,00	990	1,25	2,9	0,057
II	695	4,94	676,4	10,6	1,02	1195	1,09	2,1	0,041
II a	725, 790	4,76; 4,80	721,6		0,77	1279	1,09	1,9	0,057
II b	676	5,38	652,4		1,27	893	1,53	3,3	0,107
III	806	5,02	772,0	9,7	1,29	1270	1,25	2,6	0,058
III a	808, 895	4,88; 4,93	810,7		1,05	1328	1,26	2,7	0,067
III b	792	5,35	752,5		1,38	1003	1,55	3,4	0,104
IV	658	4,87	632,1	−17,3	0,68	1052	0,96	1,6	0,035
IV a	640	4,72	617,6		0,54	1144	0,96	1,9	0,035
IV b	625	5,07	612,0		0,81	876	1,13	2,4	0,042
V	765	4,95	750,9	5,1	0,98	1153	0,97	1,9	0,031
V a	838	4,72	786,9		0,68	1267	1,08	2,1	0,045
V b	750	5,26	725,1		1,03	865	1,60	3,9	0,096
VI	870	5,01	831,2	8,5	1,07	1297	1,23	2,8	0,051
VI a	880, 968	4,78; 4,79	861,0		0,94	1595	1,38	3,5	0,070
VI b	870	5,25	818,3		1,25	1099	1,58	3,9	0,099

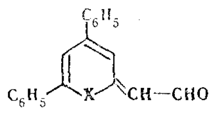
with methylamine in dimethyl sulfoxide, which, considering the solubility of the starting dyes in it and the effect on the rate of reaction of pyrylium salts with amines [6], was found to be the most suitable solvent for this transformation.



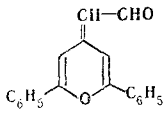
X a,b



XI a,b



XII a,b



XIII

a X=O; b X=S

Symmetrical dyes may be formed as impurities in the synthesis of unsymmetrical dyes; this would not affect the results of elementary analysis in the case under consideration. Pyrylotrimethylidynecyanine II was therefore obtained by two pathways in order to confirm its individuality. The absorption spectra of both samples had characteristics that were in complete agreement. In addition, we studied the fluorescence of solutions of this dye in methylene chloride and acetonitriles. The fluorescence spectra in these solvents were symmetrical (mirror images) to the absorption spectra and did not depend on the excitation wavelength, and this also confirmed the individuality of the dye.

The spectral characteristics of the long-wave absorption bands of dyes I-IX in methylene chloride and of dyes I-VI and Ia,b-VIa,b in acetonitrile are presented in Table 1. In additon to the generally adopted characteristics (λ_{max}, log ε, and f), the average positions of the bands (M^{-1}), their widths (σ), and the coefficients of asymmetry (γ_1), excess (γ_2), and the fine structure (F), which were obtained by mathematical treatment of the experimental bands by the method of moments, are presented in Table 1.

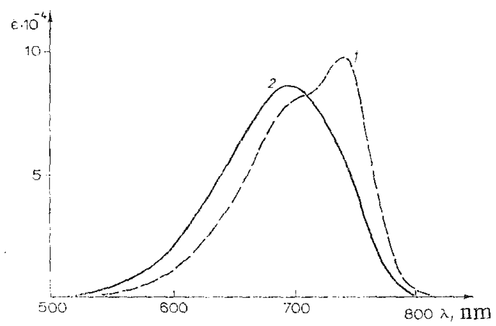


Fig. 1. Absorption curves of (2-pyrylo)(4-pyrylo)trimethylidynecyanine (II) in methylene chloride (1) and acetonitrile (2).

Let us initially examine the regularities in the positions and intensities of the bands in the spectra of carbo- and dicarbocyanines in order to exclude the effects associated with the close location of the heterocyclic residues in monomethylidynecyanines. It follows from Table 1 that unsymmetrical pyrylocarbo- and dicarbocyanines II and III, like their sulfur analogs V and VI, absorb at shorter wavelengths than their isomers of the α series and at longer wavelengths than their isomers of the γ series. Of the nitrogen-containing dyes, carbo- and dicarbocyanines VIII and IX also absorb in the region between the absorption of symmetrical dyes, except that in this case the dyes of the γ series are more deeply colored than those of the α series [2]. This is associated with the lower tendency for conjugation of the oxygen and sulfur atoms as compared with the nitrogen atom, as a consequence of which the carbon–carbon bonds of the α-pyrylium and particularly the α-thiopyrylium residues in the examined unsymmetrical dyes, like the symmetrical dyes, participate to a greater extent in the overall conjugation system than the same bonds in the analogous pyridocyanines. The intermediate length of the chromophore system in the unsymmetrical dyes as compared with the symmetrical dyes is also the principal factor that determines their color. This explanation is possible because in the examined dyes the electron-donor character of the heterocyclic residues depends only slightly on whether they are connected to the polymethine chain by means of their α or γ position [3]. The factors that determine the spectral properties of dyes I-IX therefore should be primarily the same as those in the case of dyes with symmetrical structures. For the same reason, the vinylene shifts of their absorption maxima and the M^{-1} moments are close to the corresponding characteristics of symmetrical dyes (∿100 nm), and regularities in the deviations are also absent (Table 1).

To verify the determining effect of the length of the polymethine chain on the color of the dyes under consideration we investigated their absorption spectra in two solvents with different polarities. Usually, the greater the electronic asymmetry of the dye, the greater the hypsochromic shift of the absorption band and the more pronounced the decrease in the vinylene shifts that are produced by an increase in the polarity of the solvent [7]. The dyes under consideration are not subject to this principle. For example, the absorption bands of unsymmetrical thiopyrylocyanines V and VI are shifted only 29.0 and 50.3 nm to the short-wave region on passing from the slightly polar methylene chloride to the strongly polar acetonitrile, as compared with 33.3 and 65.1 nm in the case of symmetrical thiopyrylocyanines of the α series Va and VIa. The vinylene shifts in this case decrease from 100.6 to 80.3 and from 99.9 to 74.1 nm, respectively. This unusual fact should also be explained by the existence in the unsymmetrical pyrylo- and thiopyrylocyanines of a shorter chromophore chain (and hence a lower degree of solvation [8]) as compared with their symmetrical isomers of the α series. It is apparent from Table 1 that the intensities (log ε and f) of the absorption bands of the unsymmetrical dyes are higher than in the case of the isomeric dyes of the α series but lower than in the case of the isomers of the γ series. This also constitutes evidence for the intermediate length of the chromophore of dyes I-IX.

Thiopyrylo- and pyridomonomethylidynecyanines IV and VII constitute an exception to the above-described regularity in the position of the bands. Unsymmetrical thiopyrylomonomethylidynecyanine IV absorbs not only more deeply than its symmetrical isomer of the γ series IVb but also more deeply than the isomer of the α series IVa. This is due to heightening of the color of symmetrical dye IVa due to interaction of the unbonded sulfur atoms in it [2]. Deepening of the color on passing from symmetrical isomer of the γ series VIIb to unsymmetrical dye VII and then to symmetrical isomer of the α series VIIa is observed in the series of pyridomonomethylidynecyanines. This sequence, which is the reverse of what is observed for

TABLE 2. Characteristics of the Synthesized Compounds

Compound	mp, °C (crystallization solvent)	Found, %		Empirical formula	Calc., %		Yield, %
		Cl	S(N)		Cl	S(N)	
II	275—276 [acetic acid–acetic anhydride (1:2)]	5,8		$C_{37}H_{27}ClO_6$*	5,9		45
II	275—276 (the same)	5,7		$C_{37}H_{27}ClO_6$	5,9		63
IV	234—235 (acetic acid)	5,7	10,4	$C_{35}H_{25}ClO_4S_2$	5,8	10,5	69
V	255—256 [acetic acid–acetic anhydride (1:1)]	5,4	9,7	$C_{37}H_{27}ClO_4S_2$	5,6	10,1	72
VI	194—195 (acetic anhydride)	5,4	9,2	$C_{39}H_{29}ClO_4S_2$	5,4	9,7	32
VII	136 (ethanol with added methylamine)	5,7	(4,4)	$C_{37}H_{31}ClN_2O_4$	5,9	(4,6)	76
VIII	167 (methanol with added methylamine)	5,8	(4,3)	$C_{39}H_{33}ClN_2O_4$	5,7	(4,4)	77
IX	[ethanol – acetonitrile (3:1) with added methylamine]	5,2	(4,8)	$C_{41}H_{35}ClN_2O_4$	5,4	(4,3)	26

*Found: C 73.7; H 4.2%. Calculated: C 73.7; H 4.5%.

the higher vinylogs, can be linked with an increase in the steric hindrance in the indicated series of dyes; this is in agreement with the simultaneous decrease in the extinctions and oscillator forces.

Let us now examine the regularities in the form of the bands of the investigated dyes. Replacement of methylene chloride by acetonitrile leads to a change in the ratios of the intensities of the long- and short-wave absorption maxima of dyes I-VI, as is apparent from Fig. 1 in the case of (2-pyrylo)(4-pyrylo)carbocyanine (II). Proceeding from the mirror-image character of the absorption and fluorescence spectra, it may be concluded that both maxima belong to the same electron transition. The change in the intensities of the peaks is due to intensification of the vibron interactions, which is a consequence of the increase in the electronic asymmetry of the dyes on passing to a more polar solvent, which also leads to an increase in the deviations (D_M).

The absorption bands of the unsymmetrical dyes were found to be broader than the bands of the symmetrical dyes of the γ series but narrower than the absorption bands of the dyes of the α series. This is an extremely unexpected fact, since the transition from symmetrical dyes to unsymmetrical dyes is accompanied by intensification of alternation of the C–C bonds of the polymethine chain, which leads to intensification of the vibron interactions [9] and broadening of the bands. However, quantum-chemical analysis of the quadratic changes in the bond orders during excitation (δ) [9] showed that the δ values for unsymmetrical dyes I-IX are lower than for the 2-substituted isomers and greater than for the 4-substituted isomers. For example, for pyrylocarbocyanines II and IIa,b the quadratic changes in the bond orders (calculated with the same values of the quantum-chemical parameters as in [3]) were found to be, respectively, 0.1543, 0.1762, and 0.1158. An analysis of the changes in the orders of the individual bonds showed that the intensification of the vibron interactions for the 2-substituted isomers is due to the sharp decrease in the order of the C_3–C_4 bond during excitation, which significantly exceeds the change in the orders of all of the other bonds, as a consequence of which it makes a substantial contribution (approximately one third) to the overall δ value. Replacement of one of the terminal groups in these dyes by an isomeric group leads to disappearance of one of the indicated bonds, a consequence of which is also contraction of the absorption bands of unsymmetrical dyes I-IX. The existence of a C_3–C_4 bond, the order of which decreases markedly upon excitation, in the unsymmetrical dyes gives rise to additional broadening of their absorption bands as compared with the bands of the symmetrical dyes of the γ series. This assertion follows from the fact that the electronic asymmetry of dyes I-IX is too insignificant to give rise to such large broadenings (the absorption bands of the unsymmetrical dyes are several hundred reciprocal centimeters broader than the bands of the 4-substituted isomers). In fact, the width of the absorption bands of the unsymmetrical dyes constructed from pyrylium and thio- and selenopyrylium rings joined to the chromophore at the 4 position, which have the same electronic asymmetry but do not have bonds that are capable of undergoing a marked change in their order upon excitation, is only several tens of reciprocal centimeters greater than the width of the bands of the parent dyes [8].

An increase in the polarity of the medium for both the unsymmetrical and symmetrical dyes causes widening of the bands, the magnitude of which increases rapidly as the length of the polymethine chain is increased (Table 1); in the case of the higher vinylogs replacement of methylene chloride by acetonitrile gives rise to a considerably smaller degree of broadening of the bands in dye series I-VI than in the case of their symmetrical isomers of the α series. Thus it reaches 523 cm^{-1} in the case of α-thiopyrylodicarbocyanine (VIa), as compared with 353 cm^{-1} in the case of unsymmetrical dye VI. This also constitutes evidence that dyes Ia-VIa, which have a longer chromophore chain because of the participation of the heterocyclic C—C bonds in conjugation, are solvated more strongly than the unsymmetrical dyes.

The characteristics of the form of the bands, viz., the coefficients of asymmetry, excess, and the fine structure, generally have, as one should have expected for unsymmetrical carbo- and dicarbocyanines, lower numerical values than those for the corresponding unsymmetrical compounds.

EXPERIMENTAL

The moments of the absorption bands of the dyes were determined as in [2] on the basis of the absorption spectra measured with an SF-4A spectrophotometer. The error in the measurement of the absorption spectra of dyes I, Ib-IX, and IXb was no less than two orders of magnitude in intensity, as compared with 1.5 orders of magnitude for Ia-IXa. The numerical values in Table 1 are presented with an accuracy corresponding to the degree of the error in the measurement of the spectra of the dyes. The purity of the preparations was monitored by thin-layer chromatography (TLC) on Silufol UV-254 plates with elution by acetonitrile.

2-[3-(2,6-Diphenylpyran-4-ylidene)propen-1-yl]-4,6-diphenylpyrylium Perchlorate. A) A mixture of 0.173 g (0.5 mmole) of 2-methyl-4,6-diphenylpyrylium perchlorate (Xa) and 0.137 g (0.5 mmole) of 2,6-diphenyl-4-formylmethylene-4H-pyran (XIII) was heated in 4 ml of a mixture of acetic acid and acetic anhydride (1:1) at 100°C for 30 min, after which 0.135 g of bronze crystals was removed by filtration (Table 2).

B) A mixture of 0.16 g (0.5 mmole) of 4-methyl-2,6-diphenylpyrylium tetrafluoroborate and 0.14 g (0.5 mmole) of 4,6-diphenyl-2-formylmethylene-2H-pyran (XIIa) in 2 ml of acetic anhydride with four drops of pyridine was refluxed for 2 min, after which 0.176 g of bronze crystals was removed by filtration and reprecipitated from 20 ml of acetonitrile by the addition of 20% $HClO_4$.

2-[(2,6-Diphenylthiopyran-4-ylidene)methyl]-4,6-diphenylthiopyrylium Perchlorate (IV). A mixture of 0.16 g (0.5 mmole) of 2-methyl-4,6-diphenyl thiopyrylium perchlorate (Xb) and 0.155 g (0.58 mmole) of 2,6-diphenyl-1-thio-4H-pyran-4-one in 3 ml of acetic anhydride was refluxed for 30 min, after which 0.175 g of the dye was removed by filtration.

2-[3-(2,6-Diphenylthiopyran-4-ylidene)-1-propenyl]-4,6-diphenylthiopyrylium Perchlorate (V). This compound was obtained from 0.18 g (0.5 mmole) of 4-methyl-2,6-diphenylthiopyrylium perchlorate (XIb) and 0.145 g (0.5 mmole) of 4,6-diphenyl-2-formylmethylene-1-thio-2H-pyran (XIIb) by a method similar to that used to prepare II.

2-[5-(2,6-Diphenylthiopyran-4-ylidene)-1,3-pentadienyl]-4,6-diphenylthiopyrylium Perchlorate (VI). 2-(4-Ethoxy-1,3-butadienyl)-4,6-diphenylthiopyrylium perchlorate was obtained in 70% yield as bronze crystals from 0.36 g (1 mmole) of salt Xb and 0.88 g (4 mmole) of tetraethoxypropane in 10 ml of a mixture of acetic acid and acetic anhydride (1:1) by a method similar to that used to prepare its pyrylium analog [2]. The product was used without further purification. A mixture of 0.31 g (0.7 mmole) of the derivative obtained and 0.24 g (0.67 mmole) of salt XIb in 2 ml of acetic anhydride containing 0.1 ml of pyridine was refluxed for 2 min, after which bronze crystals were removed by filtration.

1-Methyl-4-[(1-methyl-4,6-diphenyl-1,2-dihydropyridin-2-ylidene)methyl]-2,6-diphenylpyridinium Perchlorate (VII). A mixture of 0.2 g (0.35 mmole) of pyrylocyanine I and 0.5 ml of a 5% methanol solution of methylamine (0.7 mmole) in 2 ml of DMSO was heated at 100°C for 20 min, after which it was cooled, and the dye was precipitated with an aqueous solution of sodium perchlorate and purified by chromatography on aluminum oxide from acetonitrile.

1-Methyl-4-[3-(1-methyl-4,6-diphenyl-1,2-dihydropyridin-2-ylidene)-1-propenyl]-2,6-diphenylpyridinium Perchlorate (VIII). This compound was obtained from 0.15 g (0.25 mmole) of pyrylocyanine II by a method similar to that used to prepare VII.

1-Methyl-4-[5-(1-methyl-4,6-diphenyl-1,2-dihydropyridin-2-ylidene)-1,3-pentadienyl]-2,6-diphenylpyridinium Perchlorate (IX). This compound was obtained from 0.11 g (0.175 mmole) of pyrylocyanine III by a method similar to that used to prepare VII.

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2-BENZOPYRYLIUM SALTS.

26.* RECYCLIZATION OF 2-BENZOPYRYLIUM SALTS TO α-NAPHTHOLS

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The behavior of 2-benzopyrylium salts with a CH_2 group in the 1 position at pH $\leqslant 7$ was studied, and it was established that they undergo recyclization to α-naphthols under these conditions. A mechanism for the conversion is proposed. One of the intermediates, viz., 3-hydroxy-1-tetralone, was isolated.

It has been proposed [2, 3] that an equilibrium between the cationic form of the pyrylium salt and its anhydro and pseudo bases, which has been studied at pH $\geqslant 7$ [4-6] and determines its reactivity, may also exist in an acidic medium.

We have observed that, probably owing to this equilibrium, irreversible recyclization of 2-benzopyrylium salts to α-naphthols is possible at pH $\leqslant 7$. This transformation takes place to give the products in 75-90% yields when 2-benzopyrylium salts with a CH_2 group in the 1 position are heated in ethanol or water both with and without acidification.

The recyclization evidently takes place due to reaction of the pyrylium salt with water, which can add immediately to the cation, acting as a nucleophile (pathway A), or initially as a base to deprotonate it (pathway B).

The anhydro bases (benzylideneisochromenes III) formed by pathway B are derivatives of vinyl ethers, which, as is known [7], are readily hydrated in acidic media; protonation of the β-cation atom of the vinyl fragment (hydration of the exocyclic double bond is more likely) takes place with simultaneous attack by the nucleophile at the α-position, i.e., in this case the I → III transformation is irreversible. Pseudo bases IVa-i undergo subsequent recyclization to naphthols VIIa-i (R^3 = H) through 1,5-dicarbonyl compounds V.

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*See [1] for communication 25.

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