PYRYLOCYANINES. 11.* SYMMETRICAL TETRAPHENYL-SUBSTITUTED PYRYLO-2-CYANINES

M. A. Kudinova, N. A. Derevyanko,
G. G. Dyadyusha, A. A. Ishchenko,
and A. I. Tolmachev

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Symmetrical polymethine dyes (monomethylidyne, carbo-, and dicarbocyanines), viz., 4,6-diphenylpyrylium, -thiopyrylium, and -pyridinium derivatives, were synthesized. It follows from a comparison of the absorption spectra of pyrylo-2-cyanines and their heteroanalogs with the spectra of the corresponding 4 isomers that these dyes differ from one another with respect to the positions, intensities, and forms of the bands. The pyrylocarbo- and -dicarbocyanines and their sulfur analogs are more deeply colored than their γ isomers, while the reverse regularity is observed in the pyridocyanine series. The long-wave bands in the spectra of all of the α isomers are accompanied by more intensive transitions to the vibrational sublevels than in the case of the γ isomers.

In contrast to pyrylo-4-cyanines [2-6], pyrylo-2-cyanines have not yet been systematically investigated, although dyes of this type were mentioned a long time ago in [7]. It is known that solutions of some pyrylo-2-cyanines can be used as passive shut-off devices for lasers [8], and the photochemical stabilities of a number of tricarbocyanines of this type have also been studied [9]. From data on the spectral properties of these dyes it has been reported only that a tetraphenyl-substituted α-pyrylomonomethylidynecyanine absorbs in a longer-wave region and with a lower intensity than its isomer of the γ series [10]. Up until now there has been no clear information even with respect to the effect of replacement of the oxygen atoms by sulfur atoms on the color in the α-pyrylocyanine series. According to the available data [11-13], one might have concluded that this sort of replacement in the case of a tetraphenyl-substituted pyrylo-2-trimethylidynecyanine would give rise to a bathochromic shift of only 10 or 20 nm of the absorption maximum, although our quantum-chemical estimate shows that a significantly greater effect should be expected [14].

Within the framework of our systematic study of pyrylocyanines it seemed of interest to synthesize pyrylo-2-cyanines and their sulfur- and nitrogen-containing analogs in order to compare the spectral properties of these dyes and isomeric compounds in which the heterocyclic residues are connected to the polymethine chain in the 4 positions. The results of a study of symmetrical α-pyrylocyanines and their analogs are described in the present paper (Table 1).

Salts with Ia,b, IIa,b, and III structures were used in the synthesis of the investigated dyes. 2-(4-Ethoxy-1,3-butadien-1-yl)-4,6-diphenylpyrylium perchlorate (III) was obtained by condensation of 2-methyl-4,6-diphenylpyrylium perchlorate (Ia) with 1,1,3,3-tetraethoxypropane (see scheme on following page).

Monomethylidynecyanine IVa was synthesized in 42% yield by condensation of salts Ia (Y = Cl) and IIa in a mixture of acetic anhydride with acetic acid in the presence of triethylamine, although a dye cannot be obtained when sodium acetate is used in place of triethylamine, according to the data in [10]. Thiopyrylomonomethylidyne-cyanine VIIa was synthesized by the same method from salts Ib and IIb. Pyrylotrimethylidyne-cyanine Va was obtained by condensation of salt Ia with ethyl orthoformate by a method similar to that used for its thio analog VIIIa [11]. We were able to synthesize pyrylodicarbocyanine VIa only by condensation of pyrylium salt Ia with ethoxybutadienyl derivative III, while the thio analog (IXa) of this dye was obtained by

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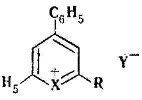
*See [1] for Communication 10.

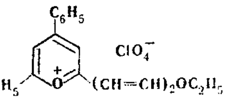
Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev 252660. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 898-902, July, 1980. Original article submitted August 6, 1979.

TABLE 1. Characteristics of the Long-Wave Absorption Bands of Solutions of Dyes IVa,b-IXa,b in Methylene Chloride

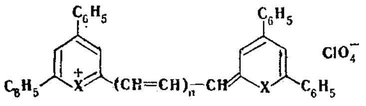
Dye	X	n	λ_{max}, nm	lg ε	M^{-1}, nm	f	σ, cm^{-1}	γ_1	γ_2	F
IVa	O	0	636	4,84	596,6	0,76	1346	1,14	2,3	0,061
IVb			555	5,15	541,3	1,00	936	1,22	3,0	0,054
Va	O	1	730; 800	4,77; 4,93	739,6	0,78	1176	1,17	2,2	0,064
Vb			686	5,40	665,1	1,21	801	1,57	3,3	0,105
VIa	O	2	820; 910	4,91; 5,08	839,5	1,12	1137	1,32	2,9	0,083
VIb			806	5,50	775,0	1,33	811	1,77	4,5	0,131
VIIa	S	0	646	4,86	622,3	0,71	1154	0,94	2,2	0,035
VIIb			630	5,12	617,4	0,83	809	1,13	2,9	0,047
VIIIa	S	1	865	4,85	820,2	0,79	1058	1,07	1,8	0,046
VIIIb			762	5,39	743,2	1,16	729	1,53	3,2	0,100
IXa	S	2	905; 1000	4,85; 5,03	926,1	0,97	1072	1,25	2,7	0,062
IXb			889	5,45	856,4	1,22	768	1,65	3,9	0,110
Xa	NCH_3	0	540	4,51	515,7	0,45	1560	1,3	3,2	0,059
Xb			515	4,93	509,8	0,66	920	0,8	1,9	0,033
XIa	NCH_3	1	630	4,97	604,6	0,88	1060	1,0	2,0	0,041
XIb			644	5,27	627,9	1,20	870	1,8	5,4	0,096
XIIa	NCH_3	2	728	—	701,8	—	1023	1,5	4,3	0,073
XIIb			758	—	736,0	—	930	2,0	6,5	0,119



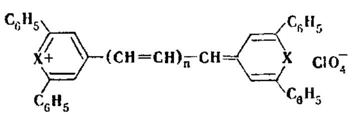
I-II a,b



III



IV-XII a



IV-XII b

Ia, b $R=CH_3$, $Y=ClO_4$ (or Cl); IIa $R=SC_2H_5$, $Y=BF_4$; IIb $R=SCH_3$, $Y=CH_3SO_4$.
a X=O; b X=S. See Table 1 for X and n for dyes IV-XII.

the usual method, viz., by condensation of thiopyrylium salt Ib with malonaldehyde dianil hydrochloride. Symmetrical pyridomono-, -carbo-, and -dicarbocyanines Xa-XIIa were obtained by treatment of pyrylocyanines IVa-VIa with methylamine.

The spectral characteristics of the synthesized α-pyrylocyanines and their sulfur- and nitrogen-containing analogs with the corresponding characteristics of the isomeric dyes in which the heterocyclic residues are connected to the polymethine chain in the γ position are compared in Table 1. In addition to the generally accepted characteristics of the long-wave absorption bands (λ_{max}, log ε, and f), the average positions of the absorption bands (M^{-1}), the characteristics of the form of the bands [the width (σ) and coefficients of asymmetry (γ_1) and excess (γ_2)] determined by the method of moments, and the coefficients of the fine structure (F) determined from the entropies of the spectral distributions [15] are presented in Table 1.

Let us initially examine the regularities in the absorption spectra of the carbo- and dicarbocyanines in order to exclude the effects associated with the close orientation of the heterocyclic residues in the monomethylidynecyanines. It is apparent from the data presented that pyrylo-2-cyanines (Va and VIa) and their sulfur analogs (VIIIa and IXa) are considerably more deeply colored than pyrido-2-cyanines (XIa and XIIa) but, on the other hand, somewhat more highly colored than the corresponding γ isomers. This can be qualitatively explained by the fact that because of the lower tendency for conjugation of oxygen and sulfur atoms as compared with nitrogen atoms in α-pyrylo- and particularly α-thiopyrylocyanines, the carbon–carbon bonds of the heterocyclic residues participate to a greater extent in the overall system of conjugation than in α-pyridocyanines, while the chromophore systems in the γ isomers of all of these days have the same length. Let us further note that the difference between the positions of the absorption maxima of the isomeric pyrylo- and thiopyrylocyanines is greater (≃100–110 nm) than the difference between the average positions of their absorption bands (M^{-1}) (≃65–75 nm). The reverse tendency is observed for the pyridocyanines. This regularity is due to the higher intensities of the transitions to the vibrational sublevels in the case of the α isomers as compared with the γ isomers, which leads to considerable broadening of their absorption bands, a consequence of which is a decrease in the extinctions and oscillator forces, as well as the coefficients of asymmetry, excess, and the fine structure. The change in these coefficients constitutes evidence for more symmetrical, flattened, and diffuse character of the absorption bands of the α derivatives as compared with the bands of the γ isomers.

In the examined series of dyes replacement of the oxygen atoms by sulfur atoms, despite the conclusions that can be drawn on the basis of the literature data [11-13], gives rise to approximately the same bathochromic shift of the absorption bands ($\Delta M^{-1} = 80$ mm) as in the series of isomeric pyrylo-4-cyanines [16]. This replacement also leads to contraction of the bands accompanied by a change in the coefficients of asymmetry, excess, and the fine structure in the same direction. Similar replacement in the series of isomeric dyes leads to analogous changes in the form of their absorption bands. The transition from pyrylo-2-cyanines to pyrido-2-cyanines is accompanied by a hypsochromic effect ($\Delta M^{-1} \simeq 135$ nm) that exceeds the analogous effect in the series of γ isomers by a factor greater than three. In addition, similar replacement leads to contraction of the absorption bands, whereas it leads to broadening of the bands in the series of γ isomers. The change in the widths of the bands on passing from pyrylocyanines to thiopyrylo- and pyridocyanines can be explained by a decrease in the vibronic interaction, approximate estimates of which can be obtained within the framework of the simple Hückel MO method [17].

In contrast to the corresponding γ isomers, contraction of the absorption bands not only on passing from monomethylidynecyanines to carbocyanines but also to dicarbocyanines is observed in the case of α-pyrylo- and α-pyridocyanines as the length of the polymethine chain increases. This constitutes evidence that the widths of the bands of these dyes are determined to a greater extent by a change in the vibronic interactions than by the solvation effect of the solvent. On the other hand, in the case of 2-thiopyrylocyanines, like the corresponding 4 isomers, the transition from carbo- to dicarbocyanines is accompanied by broadening of the absorption bands, which can be explained by predominance of the solvation effects, since these dyes contain low-basicity terminal heterocyclic groups [16].

α-Thiopyrylo- and α-pyridomonomethylidynecyanines (VIIa and Xa) constitute an exception to the regularities in the positions of the bands described above. Thiopyrylomonomethylidynecyanine VIIa absorbs slightly more deeply than its oxygen analog (IVa) and the γ isomer (VIIb). In addition, an anomalously large difference ($\Delta\lambda = 219$ nm, $\Delta M^{-1} = 198$ nm) is observed between the absorption of this dye and its higher vinylog. A similar phenomenon, the possible reason for which is interaction of the unbonded sulfur atoms, was recently observed in the isobenzothiopyrylocyanine series [1]. Of course, a certain increase, although to a considerably lesser extent, in the first vinylene shift is also observed for α-pyrylocyanines IVa and Va ($\Delta M^{-1} = 143$ nm).

In contrast to the first vinylene shift, the second vinylene shift in both the α-pyrylocyanine and α-thiopyrylocyanine series is close to the shift characteristic for symmetrical polymethine dyes (~ 100 nm). The first vinylene shifts of pyrylo- and thiopyrylocyanines are close to one another in the series of γ isomers. These facts are in agreement with the assumption of interaction of the unbonded sulfur atoms in α-thiopyrylomonomethylidyne cyanine VIIa.

Tetraphenyl-substituted pyrido-2-monomethylidynecyanine Xa is more deeply colored than the corresponding 4 isomer (Xb), in contrast to its higher vinylogs XIa and XIIa and unsubstituted pyrido-2-monomethylidynecyanine [18]. The latter can be associated with steric hindrance in monomethylidynecyanine molecule Xa, which is in agreement with the somewhat depressed value of the first vinylene shift in the series of examined α-pyridocyanines, as well as with the low, low values of the extinctions and oscillator forces for Xa. In contrast to the higher vinylogs, the wider band observed for α-pyridomonomethylidynecyanine Xa than for the case of its oxygen-containing analog is probably due to the same reason.

Specific effects associated with the close orientation of the heterocyclic residues do not influence the color of α-pyrylomonomethylidynecyanine IVa.

Thus, it follows from a comparison of the absorption spectra of pyrylo-2-cyanines and their heteroanalogs with the corresponding 4 isomers that these dyes differ markedly from one another not only with respect to the positions and intensities of the bands but also with respect to the forms of the bands.

EXPERIMENTAL

The moments of the absorption bands were determined as in [5] on the basis of the absorption spectra recorded through 200 cm^{-1} with an SF-4A spectrophotometer (with an SF-8 spectrophotometer in the case of VIIIa and IXa) of solutions in methylene chloride stabilized with 1% ethanol at layer thicknesses of 1 and 5 cm. The error in the measurement of the absorption spectra of solutions of dyes IVa,b-IXa,b was no less than two orders of magnitude (in intensity), as compared with 1.4 orders of magnitude in the case of Xa,b-XIIa,b.

TABLE 2. Characteristics of III-XII

Compound	mp, °C	Found, %		Empirical formula	Calc., %		Yield, %
		Cl	N(S)		Cl	N(S)	
III	211[a]	7,9		$C_{23}H_{21}ClO_6$[b]	8,3		71
IVa	226[a]	6,0		$C_{35}H_{25}ClO_6$	6,2		42
Va	168—170[c]	5,7		$C_{37}H_{27}ClO_6$	5,9		43
VIa	177—179	5,7		$C_{39}H_{29}ClO_6$[b]	5,6		18
VIIa	272[c]	5,8	(10,3)	$C_{35}H_{25}ClO_4S_2$	5,8	(10,3)	83
VIIIa	238[c]	5,3	(9,6)	$C_{37}H_{27}ClO_4S_2$	5,6	(10,1)	82
IXa	205—206[c]	5,3	(9,3)	$C_{39}H_{29}ClO_4S_2$	5,3	(9,7)	21
Xa	—[d]	5,9	4,6	$C_{37}H_{31}ClN_2O_4$	5,9	4,6	16
XIa	238—239[e]	5,6	4,4	$C_{39}H_{33}ClN_2O_4$	5,6	4,4	43
XIIa	201	5,4	4,4	$C_{41}H_{35}ClN_2O_4$	5,4	4,3	64

[a] From acetic acid. [b] The compositions of III and VIa were also confirmed by determination of the C and H content. [c] From acetonitrile. [d] From a mixture of alcohol with methylamine. [e] From a mixture of ethanol with acetonitrile (3 : 1).

The numerical values in Table 1 are presented with an accuracy corresponding to the error in the measurements of the absorption spectra of the dyes. The purity of the preparations was monitored by thin-layer chromatography (TLC) on Silufol-254 plates (elution with acetonitrile).

2-(4-Ethoxy-1,3-butadien-1-yl)-4,6-diphenylpyrylium Perchlorate (III). A mixture of 35 mg (0.1 mmole) of perchlorate Ia and 88 mg (0.4 mmole) of tetraethoxypropane in 4 ml of a mixture of acetic anhydride and acetic acid (1 : 1) was refluxed for 2 min, after which perchlorate III was removed by filtration. The characteristics of this compound and all of the synthesized compounds are presented in Table 2.

2-[(4,6-Diphenyl-2-pyranylidene)methyl]-4,6-diphenylpyrylium Perchlorate (IVa). A mixture of 0.150 g (0.5 mmole) of 2-methyl-4,6-diphenylpyrylium chloride and 0.190 g (0.5 mmole) of salt IIa, obtained from 4,6-diphenylpyran-2-thione and triethyloxonium tetrafluoroborate in dry methylene chloride after standing at room temperature for 3 min, was heated in 2 ml of acetic anhydride, 0.2 ml of acetic acid, and 0.1 ml of triethylamine at 145-155°C for 15 min. It was then cooled and treated with ether, and the dye was removed by filtration and converted to the perchlorate by the action of an alcohol solution of sodium perchlorate on an acetic acid solution of it.

2-[3-(4,6-Diphenyl-2-pyranylidene)prop-1-en-1-yl]-4,6-diphenylpyrylium Perchlorate (Va). This compound was obtained from 0.173 g (0.5 mmole) of salt Ia, 0.150 g (1 mmole) of ethyl orthoformate, and 0.05 g of anhydrous sodium acetate by heating in 3 ml of a mixture of acetic anhydride with acetic acid (1 : 1) at 110-115°C for 1 h.

2-[5-(4,6-Diphenyl-2-pyranylidene)penta-1,3-dien-1-yl]-4,6-diphenylpyrylium Perchlorate (VIa). A mixture of 0.35 g (1 mmole) of perchlorate Ia and 0.43 g (1 mmole) of ethoxy derivative III in 4 ml of acetonitrile with the addition of one drop of pyridine was refluxed for 1 min, after which the fine bronze-brown crystals were removed by filtration and washed on the filter with a mixture of acetic anhydride with acetic acid (1 : 1).

2-[5-(4,6-Diphenyl-2-thiopyranylidene)penta-1,3-dien-1-yl]-4,6-diphenylthiopyrylium Perchlorate (IXa). pound was obtained from 0.2 mmole of salt Ib, 0.2 mmole of 2-thylthio-4,6-diphenylthiopyrylium methylsulfate, and 0.2 mmole of anhydrous sodium acetate by heating in 2 ml of glacial acetic acid at 110-120°C for 30 min.

2-[5-(4,6-Diphenyl-2-thiopyranylidene)penta-1,3-dien-1-yl]-4,6-diphenylthiopyrylium Perchlorate (IXa). This compound was obtained from salt Ib and malonaldehyde dianil hydrochloride under the conditions used in the preparation of dye Va.

1-Methyl-2-[(1-methyl-4,6-diphenyl-1,4-dihydro-2-pyranylidene)methyl]-4,6-diphenylpyridinium Perchlorate (Xa). A mixture of 0.115 g (0.2 mmole) of pyrylocyanine IVa and 1 ml (0.5 mmole) of a 1.5% methanol solution of methylamine in 1 ml of dimethylformamide (DMF) was heated at 100-110°C for 2 h, after which it was cooled, and the dye was precipitated with an aqueous solution of sodium perchlorate. The product was purified by chromatography on aluminum oxide (elution with chloroform). The zone containing the dye was separated and eluted with alcohol—chloroform (2 : 1), after which a solution of the dye in methanol was treated with an aqueous solution of sodium perchlorate.

1-Methyl-2-[3-(1-methyl-4,6-diphenyl-1,4-dihydro-2-pyranylidene)prop-1-en-1-yl]-4,6-diphenylpyridinium Perchlorate (XIa). A mixture of 0.33 mmole of pyrylocyanine Va with 7 ml (3.5 mmole) of a 1.5% methanol solution of methylamine in 5 ml of dimethyl sulfoxide was heated at 85°C for 30 min, after which the dye was precipitated with an aqueous solution of sodium perchlorate. The product was removed by filtration and washed with a small amount of alcohol and ether.

Pyridocyanine XIIa. This compound was obtained from the corresponding pyrylocyanine VIa under the conditions used in the preparation of XIa.

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