PYRYLOCYANINES.

19.* SYMMETRICAL PYRYLOCYANINES BASED ON 3,4-POLYMETHYLENE-2,6-DIPHENYLPYRYLIUM SALTS

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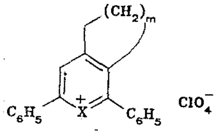
Symmetrical 2,6,2',6'-tetraphenyl-substituted pyrylo-4- and thiopyrylo-4-cyanines in which both α positions of the polymethine chain are bonded to the β positions of the heterocyclic residues by ethylene or trimethylene groups were synthesized. The introduction of bridged groupings gives rise to a bathochromic effect, which is greater for ethylene groups than for trimethylene groups.

Tetraphenyl-substituted pyrylo-2-cyanines in which the carbon atoms in the α positions of the polymethine chromophore and in the β positions of the heterocyclic residues are bonded by ethylene or trimethylene groupings were investigated in [2]. The isomeric pyrylo-4-cyanines were synthesized in order to investigate the effect of bridged groupings on the colors of the compounds. Data on dyes of this type are limited to a patent [3] in which substituted pyrylo-4-tricarbocyanines that contain trimethylene groupings are described, and the possibility of their use for the passive modulation of the quality factor of an Nd^{3+}-glass laser is demonstrated. In the present research we synthesized pyrylo-4-cyanines on the basis of diphenyl-substituted cyclopenta[c]pyrylium (Ia) and 5,6,7,8-tetrahydro-2-benzopyrylium (IIa) salts, as well as thiopyrylo-4-cyanines on the basis of the sulfur analog (Ib) of the former salt.

Pyrylium salt Ia was obtained by condensation of cyclopentenylacetophenone with benzoyl chloride by a method similar to that described for its vinylog IIa. Thiopyrylium salt Ib was obtained by treatment of Ia with a solution of sodium hydrosulfide. We were unable to replace the oxygen atom by a sulfur atom in tetrahydrobenzopyrylium salt IIa. This evidently also could not be achieved in [3], since the spectral characteristics of the thio derivative presented therein were identical to the characteristics of the corresponding pyrylocyanine, whereas thiopyrylocyanines usually absorb at considerably lower values than their oxygen analogs.



Ia, b, IIa

I $m=2$; II $m=3$;
a X=O, b, X=S

The condensation of salts Ia, b and IIa with ethyl orthoformate and malonic and glutaconic aldehyde hydrochlorides was used to synthesize, respectively, pyrylocarbocyanines, pyrylodicarbocyanines, and pyrylotricarbocyanines IIIa-VIIIa with ethylene and trimethylene bridged groupings, as well as the vinylogous series of thiopyrylocyanines IIIb-Vb (Table 1). The condensations were carried out in glacial acetic acid or in a mixture of the latter with acetic anhydride in the presence of anhydrous sodium acetate. The indicated transformations proceed relatively smoothly; this is explained by the high reactivities of the starting salts and the stabilizing effect of the bridged groups on the dyes. The fact that

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*See [1] for communication 18.

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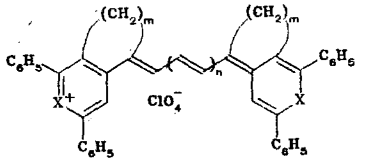
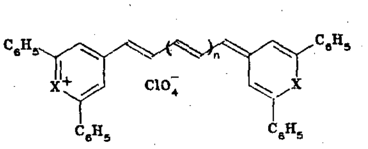
TABLE 1. Characteristics of the Long-Wave Absorption Bands of Solutions of the Dyes in Methylene Chloride

Compound	X	m	n	λ_{max}, nm	lg ε	M^{-1}, nm	f	σ, cm^{-1}	γ_1	γ_2	F
IIIa	O	2	0	750	5,42	725,2	1,10	770	1,56	3,2	0,117
IVa	O	2	1	855	5,59	823,5	1,46	780	1,96	5,8	0,141
Va	O	2	2	980	5,49	—	—	—	—	—	—
VIa	O	3	0	728	5,15	707,3	0,93	776	1,53	3,0	0,115
VIIa	O	3	1	822	5,45	795,8	1,26	784	1,90	5,6	0,138
VIIIa	O	3	2	942	5,41	—	—	—	—	—	—
IXa	O	—	0	686	5,40	665,1	1,21	801	1,57	3,3	0,105
Xa	O	—	1	806	5,50	775,0	1,33	811	1,77	4,5	0,131
IIIb	S	2	0	818	5,32	785,0	0,97	703	1,55	3,2	0,105
IVb	S	2	1	925	5,42	888,9	1,32	734	1,71	4,8	0,119
Vb	S	2	2	1052	5,44	994,2	1,39	878	1,68	4,3	0,108
IXb	S	—	0	762	5,39	743,2	1,16	729	1,53	3,2	0,100
Xb	S	—	1	889	5,45	856,4	1,22	768	1,65	3,9	0,110
XIb	S	—	2	1020	5,47	961,7	1,31	910	1,54	3,7	0,101

Balaban and Nenitzescu [4] assigned the absorption at 700 nm to salts Ia, b synthesized by a different method can be explained by the presence of admixed polymethine dyes. The stabilizing effect of bridged groups follows, for example, from the fact that, in contrast to pyrylotricarbocyanines Va and VIIIa, we were unable to obtain their analog XIa (X = O, n = 2), which does not contain bridged groups, in the analytically pure state.



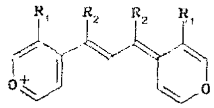
IIIa,b–VIa,b VIa–VIIIa



IXa,b–XIa,b

a X=O; b X=S

The spectral characteristics of the synthesized 4-pyrylocyanines and their thio analogs are compared with the corresponding characteristics of unsubstituted dyes IX-XI in Table 1. In addition to λ_{max}, log ε, and the oscillator forces (f), the average positions of the bands (M^{-1}), the widths (σ), and the characteristics of their form [the coefficients of asymmetry (γ_1), excess (γ_2), and the fine structure (F)] are presented. It follows from the data presented in Table 1 that the introduction of polymethine bridged groups leads to deepening of the color; the bathochromic shift for the carbocyanines (n = 0) is somewhat greater than for the dicarbocyanines (n = 1), and the effect of ethylene groups is greater than the effect of trimethylene groups. The observed effect in the γ-pyrylocyanine series is approximately the same as the effect observed for the isomeric dyes of the α series, whereas for γ-thiopyrylocyanines it is approximately half the effect observed for the α isomers [2]. The explanation for the effect of bridged groups on the color of the dyes should be sought in their electronic and steric effects. The groupings under consideration do not change the conformation of the polymethine chain of γ-pyrylocyanines, whereas they fix the di-cis conformation of the chromophore in dyes of the α series. Steric hindrance between the sulfur atoms of the heteroresidues and the hydrogen atom of the polymethine chain evidently exists in this conformation of the α-thiopyrylocyanine molecules, and this gives rise to the above-noted greater effect from the introduction of bridged groups as compared with the effect observed in the γ-thiopyrylocyanine series. There is also a certain amount of steric hindrance directly between the methylene groups of the bridges. This hindrance is manifested in a decrease in the oscillator forces for all of the pyrylo- and thiopyrylocarbocyanines with polymethine bridges as compared with the unsubstituted dyes, whereas bridged groupings cause an increase in the f values in the dicarbocyanine series. In the case of pyrylotrimethylidynecyanines a decrease in f is also accompanied by a decrease in the coefficients of asymmetry and excess; this is in agreement with the increase in the steric hindrance in the molecule. The effect under consideration increases in the case of trimethylene groups, which is also responsible to a considerable extent for the sharp decrease in the extinction at the maximum for trimethylidynecyanine VIa as compared with the extinction of unsubstituted dye IXa. As in the case of their isomers of the α series, the bridged groups in the dyes under consideration may affect not only the coplanarity of the polymethine chromophore but also the conformation of the phenyl groups in the α position of heteroresidues adjacent to the bridge by disrupting the conjugation of these groups with the overall chromophore system. An increase in the torsion angle between the planes of the phenyl substituent and the heteroring under the influence of an adjacent polymethylene group for 2,3-polymethylene-4,6-diphenylpyrylium salts that are isomeric with respect to Ia and IIa was established by PMR spectroscopy [2]. This effect should be greater for trimethylene bridges than for ethylene bridges, and this determines the decrease in the oscillator force not only for pyrylocarbocyanine VIa but also for pyrylodicarbocyanine VIIa as compared with the f values for unsubstituted dyes IXa and Xa. This effect is possibly also partly responsible for the higher color of dyes with trimethylene groupings (VIa-VIIIa) as compared with dyes with ethylene groupings (IIIa-Va).



XII

$\lambda_{\max}^{\text{theor}}$, nm, when $R_1=R_2=H$ 473, $R_1+R_2=-(CH_2)_2-$ 683, $R_1+R_2=-(CH_2)_3-$ 608

However, the effect of polymethylene groupings on the color of the dyes cannot be explained by only steric factors. Calculation of the absorption maxima of model dyes XII by the Hückel method with the same set of parameters as for their isomers of the α series [2] showed that allowance for the electronic effects of the polymethylene bridges also makes it possible to expect bathochromic shifts and that the effect of an ethylene bridge should be greater.

Thus, as in the case of the α isomers, a significant part of the effect of bridges on the positions of the absorption bands of γ-pyrylocyanines can be ascribed to the direct interaction of the electrons of the saturated groups with the unsaturated chromophore and with one another. The electronic effect of polymethylene groups as electron donors on the color of the dyes is in agreement with the Verster—Dewar—Knott rule [5].

With respect to the form of the absorption bands of the examined dyes, one's attention is directed to the fact that, as in the α-pyrylocyanine series [2], the introduction of cyclic groupings leads to contraction of the absorption bands, which in the case of dicarbocyanines is also accompanied by an increase in the asymmetry and peaked character of the bands, as evidenced by the decrease in the σ values and an increase in the γ_1 and γ_2 values. An increase in the F values in the case of cyclization indicates that the introduction of bridged groups in all of the cases examined leads to an increase in the structured character of the absorption bands; this may be associated with an increase in the rigidity of the molecules. It should be noted that the indicated principles are expressed somewhat more weakly in the γ-pyrylocyanine series than in dyes of the α series [2].

EXPERIMENTAL

The moments of the absorption bands of the dyes in methylene chloride stabilized with 1% absolute ethanol were determined as indicated in [2] with SF-4A and SF-8 spectrophotometers. The UV spectrum of salt Ib in CH_3CN with the addition of 1% 70% $HClO_4$ was measured with an SF-4A spectrophotometer. The purity of the preparation was monitored by thin-layer chromatography (TLC) on Silufol UV-254 plates by elution with acetonitrile.

1,3-Diphenylcyclopenta[c]thiopyrylium Perchlorate (Ib). A 6-ml sample of an aqueous alcohol solution of sodium hydrosulfide prepared by the method in [6] was added with stirring to a suspension of 0.4 g (1.07 mmole) of salt Ia in 15 ml acetonitrile and filtered. The filtrate was treated with 2 ml of 70% $HClO_4$, and the precipitated yellow crystals were removed by filtration and washed with acetic acid, benzene, and ether (Table 2). The crystals were purified by crystallization from acetic acid. UV spectrum, $\lambda_{\max}$ (log ε): 228 (4.21), 264 (4.34), and 3.84 nm (4.24).

1,3-Diphenyl-5-[(1,3-diphenylcyclopenteno[3,2:c]pyran-5-yl)methylidene]cyclopenta[c]pyrylium Perchlorate (IIIa) and Its Thio Analog (IIIb). These compounds were obtained from 0.2 mmole of salt Ia or Ib, respectively, 0.2 mmole of anhydrous sodium acetate, and 0.8 mmole (for IIIa) or 0.1 mmole (for IIIb) of ethyl orthoformate in 2 ml of glacial acetic acid by heating at 120°C for 30 min. The products were purified by crystallization from acetonitrile (IIIa) or acetic acid (IIIb).

TABLE 2. Characteristics of the Synthesized Compounds

Compound	mp, °C (dec.)	Found, %			Empirical formula	Calc., %			Yield, %
		C	H (S)	Cl		C	H (S)	Cl	
Ib	197—198		(8,1)	8,9	$C_{20}H_{17}ClO_4S$		(8,2)	9,0	72
IIIa	302—303	74,8	4,5	5,7	$C_{41}H_{31}ClO_6$	75,2	4,7	5,4	44
IIIb	229—230		(9,0)	—	$C_{41}H_{31}ClO_4S_2$		(9,3)	—	30
IVa	308—309	75,6	5,1	4,9	$C_{43}H_{33}ClO_6$	75,8	5,8	5,2	64
IVb	256—257		(9,0)	5,2	$C_{43}H_{33}ClO_4S_2$		(9,0)	4,9	50
Va	207—209			4,8	$C_{45}H_{35}ClO_6$			5,0	70
Vb	205—206		(8,5)	—	$C_{45}H_{35}ClO_4S_2$		(8,7)	—	54
VIa	240—243	75,7	5,2	5,3	$C_{43}H_{35}ClO_6$	75,5	5,0	5,2	26
VIIa	248—250	76,4	5,3	4,9	$C_{45}H_{37}ClO_6$	76,4	5,2	5,0	36
VIIIa	291—293			4,6	$C_{47}H_{39}ClO_6$			4,8	55

1,3-Diphenyl-5-{3-[(1,3-diphenylcyclopenteno[3,2:c]pyran-5-yl)-2-propenylidene]}cyclopenta[c]pyrylium Perchlorate (IVa) and Its Thio Analog IVb. These compounds were obtained from 0.5 mmole of salt Ia or Ib, respectively, 0.25 mmole of phenyl[(3-phenylamino)-2-propenylidene]ammonium chloride, and 0.5 mmole of anhydrous sodium acetate in 3 ml of a mixture of glacial acetic acid and acetic anhydride (1:1) by heating at 120°C for 30 min (for IVa) or by refluxing for 2 min (for IVb). The products were purified by crystallization from acetic anhydride.

1,3-Diphenyl-5-{5-[(1,3-diphenylcyclopenteno[3,2:c]pyran-5-yl)-2,4-pentadienylidene]}-cyclopenta[c]pyrylium Perchlorate (Va) and Its Thio Analog Vb. These compounds were obtained from 0.2 mmole of salt Ia or Ib, respectively, and 0.1 mmole of phenyl[(5-phenylamino)-2,4-pentadienylidene]ammonium chloride as in the preparation of IIIa. The products were purified by washing with acetic acid until the filtrate was colorless.

1,3-Diphenyl-5-[(1,3-diphenyl-6,7-dihydro-8H-2-benzopyran-5-yl)methylidene]-5,6,7,8-tetrahydro-2-benzopyrylium Perchlorate (VIa). This compound was obtained from salt IIa [7] by a method similar to that used to prepare IIIa using 0.8 mmole of pyridine in place of NaOAc. The product was purified in the same way as IIIb.

1,3-Diphenyl-5-{3-[(1,3-diphenyl-6,7-dihydro-8H-2-benzopyran-5-yl)-2-propenylidene]}-5,6,7,8-tetrahydro-2-benzopyrylium Perchlorate (VIIa). This compound was obtained from salt IIa by a method similar to that used to prepare IVa. The product was crystallized from acetic acid.

1,3-Diphenyl-5-{5-[(1,3-diphenyl-6,7-dihydro-8H-2-benzopyran-5-yl)-2,4-pentadienylidene]}-5,6,7,8-tetrahydro-2-benzopyrylium Perchlorate (VIIIa). This compound was obtained and purified by the methods used in the case of Va.

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