

PYRYLOCYANINES.

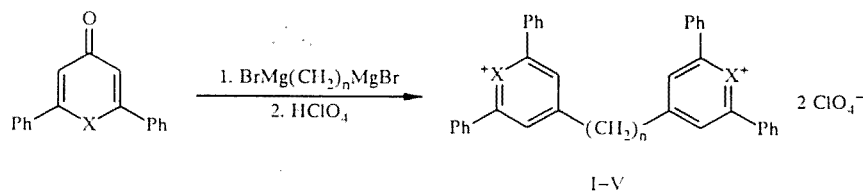
33.* PYRYLOCARBOCYANINES WITH BRIDGE GROUPS IN THE CHROMOPHORE

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Salts of 4,4-tetra-, penta-, and hexamethylene-bis-(2,6-diphenylpyrylium) and -thiopyrylium were synthesized and used as the basis for producing trimethylcyanines with ethylene, tri- and tetramethylene bridge groups in the chromophore. Factors influencing the color of these dyes were analyzed. The bis-pyrylium salts were converted to derivatives of pyridine, N-methyl- and N-phenylpyridinium. The structure of the compounds obtained was confirmed by the data of electron spectroscopy and PMR spectroscopy.

Trimethylcyanines with bridge groups in the chromophore, constructed from nitrogen-containing heterocycles, have long been known [2]. Their systematic investigation is still being continued [3, 4]. On the contrary, trimethylcyanines of a similar type — derivatives of pyrylium and thiopyrylium — had remained unknown until recently. Only recently did we describe the first representatives of them, containing benzopyrylium and benzothiopyrylium residues [5].

The aim of this work was to develop the synthesis of 2,6-diphenylpyrylo-4-carbo-cyanines and their sulfur-containing analogs with a polymethylene bridge in the chromophore. It was suggested that 4,4-polymethylene-bis-(2,6-diphenylpyrylium) and (-thiopyrylium) salts with the structure I-V be used as the starting materials. These salts were synthesized by the action of Grignard reagents produced from the corresponding dibromoalkanes on 2,6-diphenylpyrone and its thioanalog.

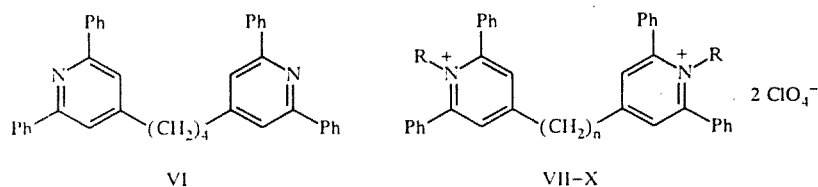


I, IV n=4; II, V n=5; III n=6; I-III X=O; IV, V X=S

In the electronic absorption spectra of the pyrylium and thiopyrylium dications I-V, like the cations of 2,6-diphenyl-4-methylpyrylium [6] and its sulfur-containing analog, bands are observed in the region 274-277, 386-389 and 263, 393-400 nm, respectively. The molecular extinction coefficients of these bands, just as we should have expected, are approximately twice as high as for the corresponding monocations. In the PMR spectra of the bis-salts, in addition to the signals of the aromatic protons, signals of protons of the methylene groups of the polymethylene chains are observed.

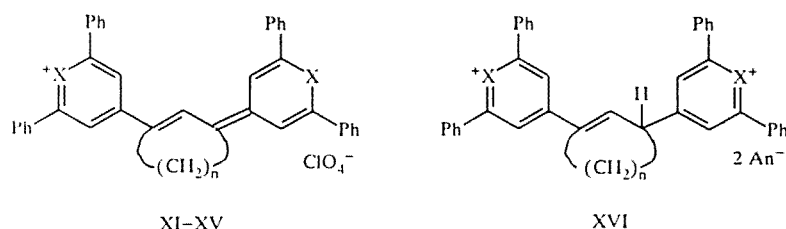
On the example of the reaction of the salt I with ammonia and that of the salts II and III with methylamine and aniline, resulting in the production of derivatives of polymethylene-bis-pyridine (VI) and -bis-pyridinium (VII-X), it was shown that the bis-pyrylium salts that we synthesized react with the indicated nucleophiles similarly to the usual pyrylium salts [7]. The electronic absorption spectra and chemical shifts in the PMR spectra of compounds VI-X are close to the corresponding characteristics of 2,6-diphenyl-4-methylpyridine and -pyridinium [6, 8].

*For communication 32, see [1].



VII $n=4$, $R=Me$; VIII $n=5$, $R=Me$; IX $n=4$, $R=Ph$; X $n=5$, $R=Ph$

In the salts I-V obtained, the activity of the α -methylene groups in the hydrocarbon fraction, as well as in their benzo-homologs [5], is lowered in comparison with the corresponding methyl-substituted salts. In contrast to the latter, their condensation with ethyl orthophormate could not be conducted. However, in the interaction of the salts I-V with diethoxymethyl acetate, which possesses higher electrophilicity, the corresponding carbocyanines XI-XV, containing di-, tri-, and tetramethylene groups in the chromophore, were obtained.



XI, XIV $n=2$; XII, XV $n=3$; XIII $n=4$; XI-XII $X=O$; XIV, XV $X=S$;
XVI $n=2, 3, 4$; $X=O, S$

From the patterns in the PMR spectra we note that the signals of the protons of the $-CH=$ group of the chromophore in the dyes XI and XIV with ethylene bridges are situated in a stronger field (δ 9.28 and 8.87 ppm) than for their analogs XII and XV with a trimethylene bridge (δ 8.61 and 8.59 ppm), which agrees with the stronger electron donor-effect of the ethylene bridge. In the spectrum of the dye XV, as a result of the low (in the NMR time scale) rate of rotation around bonds between the heteroresidues and the chromophore closed by the bridge group, nonequivalence of the two pairs of β -protons of the pyrylium residues can be observed (δ 6.47-8.17 ppm).

Table 1 presents not only the data of the PMR spectra but also the characteristics of the long-wave bands in the electronic absorption spectra of the synthesized dyes in methylene chloride. From a comparison of these values with the corresponding characteristics for analogous trimethylcyanines with an unclosed chromophore (for pyrylocarbocyanine λ_{\max} 686 nm, $\log \epsilon$ 5.40; for thiopyrylocarbocyanine λ_{\max} 762 nm, $\log \epsilon$ 5.39 [9]) it follows that, like flavilocyanines [5], for pyrylo- and thiopyrylotrimethylcyanines the cyclic groups induce a deepening of the color, and the influence of the ethylene groups is the strongest, whereas that of the trimethylene groups is the weakest. The influence of the bridge groups on the intensity of the absorption bands of pyrylocyanines XI-XV is somewhat different from that in their flavylum analogs [5]. Although both trimethylene and triethylene groups induce a drop in the intensity of the bands in the latter analogs, in the series of dyes under consideration the influence of the ethylene bridges, on the contrary, is accompanied by an increase in the intensity of the absorption bands, whereas a trimethylene bridge induces a drop in it, which is even greater in the dye XIII with a tetramethylene bridge. The deepening of the color, like the drop in the intensity of the bands in the case of pyrylocyanines XII, XIII, and XV with tri- and tetramethylene bridges, is undoubtedly associated with steric hindrances contributed by these groups. However, their electronic influence, which should also cause a deepening of the color, is also superimposed upon the steric effect. It is precisely this electronic influence, due to the formation of an unsaturated five-membered ring participating in the general conjugation system, that also explains the large bathochromic shift. Actually, judging by the values of $\log \epsilon$, in the molecules of the dyes XI and XV, in contrast to their flavylum analogs, there is no steric hindrance. All the trimethylcyanines XI-XV, analogous to pyrylocyanines with an unclosed chromophore [10], are protonated forming dications with the structure XVI when they dissolve in trichloroacetic acid. In this case, the addition of sulfuric acid is required to shift the equilibrium in the direction of the dication for the dyes XI and XIV with an ethylene bridge. The higher basicity of pyrylotrimethylcyanines with six- and seven-membered rings in the chromophore is caused by the steric hindrances in their molecules, which are eliminated upon protonation.

TABLE 1. Characteristics of the Compounds Synthesized

Compound	Empirical formula	mp, °C	Electronic spectrum, λ_{\max} , nm* (log ϵ)	PMR spectrum, δ , ppm**	Yield, %
I	C ₃₈ H ₃₂ Cl ₂ O ₁₀	233...234	241 (4,46), 277 (4,60), 386 (4,69)	1,77 (4H, m, β CH ₂); 2,86 (4H, m, α CH ₂); 7,26...7,92 (24H, s, H _{arom})	69
II	C ₃₀ H ₃₄ Cl ₂ O ₁₀	210...211	240 (4,46), 275 (4,57), 386 (4,52)	0,98 (2H, m, γ CH ₂); 1,51 (4H, m, β CH ₂); 2,73 (4H, t, α CH ₂); 7,24...7,81 (24H, m, H _{arom})	71
III	C ₄₀ H ₃₆ Cl ₂ O ₁₀	222...223	243 (4,46), 277 (4,59), 389 (4,67)	1,49 (4H, m, γ CH ₂); 1,71 (4H, m, β CH ₂); 2,98 (4H, t, α CH ₂); 7,48 (12H, m, H _{arom}); 8,07 (12H, m, H _{arom})	44
IV	C ₃₈ H ₃₂ Cl ₂ O ₈ S ₂	215...216	263 (4,76), 400 (4,53)	1,79 (4H, m, β CH ₂); 2,96 (4H, m, α CH ₂); 7,20...7,60 (20H, m, H _{Ph}); 8,27 (4H, s, H _{Het})	21
V	C ₃₀ H ₃₄ Cl ₂ O ₈ S ₂	221...222	263 (4,76), 393 (4,55)	1,63 (2H, m, γ CH ₂); 1,88 (4H, m, β CH ₂); 3,11 (4H, t, α CH ₂); 7,21...7,78 (20H, m, H _{Ph}); 8,46 (4H, s, H _{Het})	41
VI	C ₃₈ H ₃₂ N ₂	174...175	307 (4,21)	1,65 (4H, m, β CH ₂); 2,63 (4H, m, α CH ₂); 7,30...7,50 (15H, m, H _{arom}); 8,24...8,33 (9H, m, H _{arom})	30
VII	C ₄₀ H ₃₈ Cl ₂ N ₂ O ₈	169...170	295 (4,22)	1,78 (4H, m, β CH ₂); 2,90 (4H, m, α CH ₂); 3,63 (6H, s, CH ₃); 7,58 (20H, m, H _{Ph}); 7,69 (4H, s, H _{Het})	72
VIII	C ₄₁ H ₄₀ Cl ₂ N ₂ O ₈	129...130	293 (4,33)	1,46 (2H, m, γ CH ₂); 1,74 (4H, m, β CH ₂); 2,88 (4H, t, α CH ₂); 3,63 (6H, s, CH ₃); 7,58 (20H, m, H _{Ph}); 7,69 (4H, s, H _{Het})	80
IX	C ₅₀ H ₄₂ Cl ₂ N ₂ O ₈	172...173	299 (4,13)	1,77 (4H, m, β CH ₂); 2,94 (4H, m, α CH ₂); 6,75...7,85 (34H, m, H _{arom})	47
X	C ₅₁ H ₄₄ Cl ₂ N ₂ O ₈	156...157	292 (4,27)	1,15 (2H, m, γ CH ₂); 1,89 (4H, m, β CH ₂); 2,99 (4H, m, α CH ₂); 6,78...8,18 (34H, m, H _{arom})	46
XI	C ₃₉ H ₂₉ ClO ₆	253...254	759 (5,49)	2,94 (4H, m, CH ₂); 6,97 (2H, s, H _{Het}); 7,38...7,44 (12H, m, H _{Ph}); 7,85 (4H, m, H _{Ph}); 8,07 (4H, m, H _{Ph}); 8,16 (2H, s, H _{Het}); 9,28 (1H, s, H _{meso})	85
XII	C ₄₀ H ₃₁ ClO ₆	262...263	730 (5,23)	2,02 (2H, m, CH ₂ centr.); 2,59 (4H, m, CH ₂); 7,51 (14H, m, H _{arom}); 8,05 (10H, m, H _{arom}); 8,64 (1H, s, H _{meso})	90
XIII	C ₄₁ H ₃₃ ClO ₆	236...237	743 (4,92)	1,98 (4H, m, CH ₂ centr.); 2,86 (4H, m, CH ₂); 7,52 (12H, m, H _{Ph}); 7,65 (4H, s, H _{Het}); 8,21 (8H, m, H _{Ph}); 8,31 (1H, s, H _{meso})	66
XIV	C ₃₉ H ₂₉ ClO ₄ S ₂	224...225	835 (5,48)	3,00 (4H, m, CH ₂); 7,49 (14H, m, H _{arom}); 7,70 (10H, m, H _{arom}); 8,87 (1H, s, H _{meso})	81
XV	C ₄₀ H ₃₁ ClO ₄ S ₂	223...224	811 (5,17)	2,06 (2H, m, CH ₂ centr.); 2,59 (4H, m, CH ₂); 7,46 (12H, m, H _{Ph}); 7,74 (8H, m, H _{Ph}); 7,90 (4H, s, H _{Het}); 8,59 (1H, s, H _{meso})	60

*The spectra of compounds I-V, VII-X were measured in acetonitrile (in the case of I-V with an addition of 20% HClO₄, VII-X with an addition of a solution of methylamine in methanol); VI in pyridine; XI-XV in methylene chloride (stabilized by 1 % absolute ethanol).

**The spectra of compounds I-V, IX-X were recorded in a solution of CF₃COOD; VI in C₅D₅N; VII, VIII in CD₃CN; XI-XV in C₆D₅NO₂; the values in ppm were determined according to the center of the multiplets.

EXPERIMENTAL

The electronic absorption spectra of compounds I-XV were measured on a Specord M-40 spectrophotometer. The PMR spectra were measured on a Bruker WP-200 spectrophotometer with working frequency 200.132 MHz at 25°C, internal standard HMDS.

The purity of the preparations was monitored by thin-layer chromatography on Silufol UV-254 plates. Eluent acetonitrile.

The data of elementary analysis of the synthesized compounds for C, H, Cl, N, and S correspond to the calculated values.

Compounds I-IV were crystallized from a mixture of acetic acid-acetonitrile, 3:1; V, XIII-XV from acetic acid; VI from methyl propionate; VII, VIII from ethanol; IX-X from ethanol, then from acetic acid; XI, XII from a mixture of acetic acid-acetonitrile, 10:1.

4,4-Tetramethylene-bis-(2,6-diphenylpyrylium) Diperchlorate (I). To a solution of 2.48 g (0.01 mole) 2,6-diphenylpyrone in 25 ml of anhydrous tetrahydrofuran (or monoglyme), a solution of the Grignard reagent obtained from 0.5 g (0.02 g-atom) magnesium and 2.15 g (0.01 mole) 1,4-dibromobutane in 5 ml of absolute ether was added dropwise with mixing. After the end of the addition, the reaction mixture was kept for 2 h at 40°C, then the solvent was removed under vacuum, and first 2 ml of 57% perchloric acid and then 20 ml of 20% perchloric acid were added at 0°C. The precipitate of the product was filtered off and washed with acetic acid with ether.

Diperchlorates of 4,4-pentamethylene-bis-(2,6-diphenylpyrylium) (II), 4,4-hexamethylene-bis-(2,6-diphenylpyrylium) (III), 4,4-tetramethylene-bis-(2,6-diphenylthiopyrylium) (IV), and 4,4-pentamethylene-bis-(2,6-diphenylthiopyrylium) (V) were produced analogously, starting from 2,6-diphenylpyrone and 1,5-dibromopentane or 1,6-dibromopentane in the case of the salts II and III, respectively, and from 2,6-diphenylthiopyrone and 1,4-dibromobutane or 1,5-dibromopentane in the case of the salts IV and V, respectively.

4,4-Tetramethylene-bis-(2,6-diphenylpyridine) (VI). A mixture of 1 mmole of the bis-pyrylium salt I and 17 mmoles of ammonium acetate was boiled for 1 h in 10 ml of acetic acid. The reaction mixture was cooled and poured out into 100 ml of water; the precipitate that formed was filtered off and washed with water and with alcohol.

4,4-Tetramethylene-bis-(1-methyl-2,6-diphenylpyridinium) Diperchlorate (VII). A mixture of 0.4 g (0.56 mole) of the salt I, 2 ml of a 7% solution of methylamine in methanol, and 15 ml of methylene chloride was mixed at 20°C for 3 h. The solvent was removed under vacuum, and ether was added to the residue. The salt VII was filtered off and washed with ether.

4,4-Pentamethylene-bis-(1-methyl-2,6-diphenylpyridinium) Diperchlorate (VIII) was produced analogously from the salt II.

4,4-Tetramethylene-bis-(1-phenyl-2,6-diphenylpyridinium) Diperchlorate (IX). A mixture of 0.4 g (0.56 mmole) of the salt I, 0.4 g (4.3 mmoles) aniline, and 0.05 g sodium acetate in 2 ml of ethanol was boiled for 2 h, then cooled to room temperature; the product was precipitated with ether, and the precipitate was filtered off and washed with ether.

4,4-Pentamethylene-bis-(1-phenyl-2,6-diphenylpyridinium) diperchlorate (X) was produced analogously, starting with the salt II.

2,6-Diphenyl-4-[3-(2,6-diphenylpyranylidene-4)-1,3-dimethylenepropen-1-yl-1]pyrylium Perchlorate (XI). A mixture of 0.15 g (0.24 mmole) of the salt I, 0.07 g (0.5 mmole) diethoxymethyl acetate, and 0.01 g (0.15 mmole) pyridine in 1 ml of a mixture (1:1) of acetic acid with acetic anhydride was kept at 135°C for 1 h. The dye was filtered off and washed with ether.

The trimethylcyanines XII-XV were produced analogously from the salts II-V, respectively, but to obtain the dyes XIII and XV the reaction mixtures were heated for 2 min in a burner flame.

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