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PYRYLOCYANINES.

34.* PYRYLOCARBOCYANINES OF ASYMMETRICAL STRUCTURE WITH BRIDGE GROUPS IN THE CHROMOPHORE

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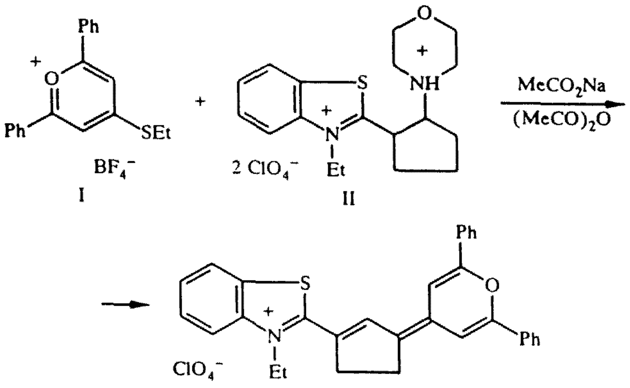
Asymmetrical carbocyanines with bridge groups in the chromophore, containing pyrylium, benzothiazolium, and pyridinium residues, were produced. The electronic and steric influence of the bridge groups on the spectral properties of the dyes was analyzed. The structure of the compounds obtained was confirmed by the data of electron spectroscopy and PMR spectroscopy.

Trimethinecyanines with a symmetrical structure with bridge groups in the chromophore, constructed from nitrogen-containing heterocycles, have long been known [2]. Recently we have described similar dyes that are pyrylium and thiopyrylium derivatives [1, 3]. Up to now, among the asymmetrical carbocyanines with bridge groups in the chromophore, dyes containing only a benzoxazole residue together with a benzothiazole, i.e., fragments that differ little in electron-donor capacity, were known [4]. In view of the small difference in the symmetry of these dyes, their absorption maxima either coincided or differed only slightly from half the sum of the absorption maxima of the corresponding dyes with a symmetrical structure (i.e., there was virtually no deviation for them). In the program of our systematic investigations in the field of polymethine dyes with bridge groups in the chromophore, in this work we undertook to investigate the influence of bridge groups on the symmetrical properties of carbocyanines possessing high electronic asymmetry. For this purpose we synthesized carbocyanines with the structures III, IV, VII, and VIII, containing pyrylium, benzothiazolium, and pyridinium residues. Thia-2,5-diphenylpyrylo-4-carbocyanine with an ethylene bridge group in the chromophore (III) was produced by condensation of 2,6-diphenyl-4-ethylmercaptopyrylium tetrafluoroborate (I) with a benzothiazolium salt with the structure II, which was synthesized analogously to its N-methyl analog [4]. When the dye III was treated with methylamine, it was converted to the corresponding asymmetrical thiapyridocarbocyanine IV.



I

II

III

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*For communication 33, see [1].

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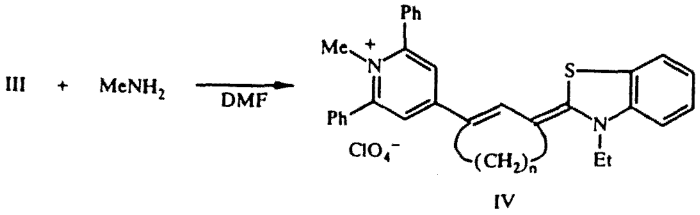
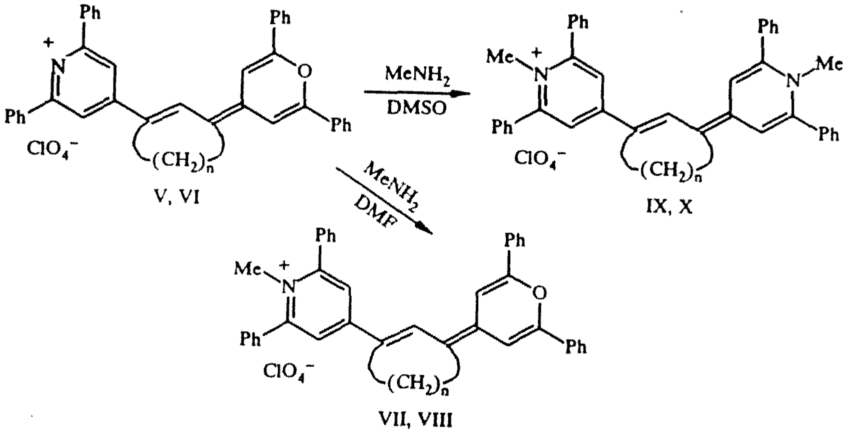


Asymmetrical pyrylopyridocarbocyanines VII and VIII, with ethylene and trimethylene bridge groups in the chromophore, could be obtained by treating the pyrylocyanines V and VI [1] with methylamine in DMFA solution. In the reaction of the same reagents, but in DMSO medium, both pyrylium residues of the pyrylocyanines are converted to pyridinium rings, as a result of which pyridocyanines with a symmetrical structure IX-X are obtained. This difference is due to the fact that in the molecule of the original asymmetrical dye formed, the positive charge is concentrated primarily on the residue of the nitrogen heterocycle, which lowers the reactivity of the molecule, whereas in DMSO medium, evidently as a result of its greater polarity and nucleophilicity [5], pyrylium salts are converted to pyridinium salts substantially more readily than in DMFA medium [6].



The structure of the symmetrical and asymmetrical trimethinecyanines synthesized was confirmed by the PMR spectra and agrees with the data of their electronic absorption spectra. From the patterns in the PMR spectra we noticed that in symmetrical pyridocyanines IX and X, just as in the symmetrical pyrylocyanines V and VI [1], as a result of the low (in the NMR time scale) rate of rotation around the bonds between the heteroresidues and the chromophore closed by a bridge group, a nonequivalence of the two pairs of β-protons of the pyridinium residues is observed (δ 6.51 and 7.05 ppm for IX and δ 6.75 and 6.98 ppm for X). On the contrary, in the asymmetrical carbocyanines VII and VIII, this nonequivalence is observed only for the β-protons of the pyrylium residues (δ 6.46 and 6.98 ppm for VII and δ 6.82 and 7.21 ppm for VIII), whereas for the pyridinium residues the signals of the two β-protons merge into one common signal (δ 7.42 ppm for VII and 7.77 ppm for VIII). This may be explained by a decrease in the order of the bonds between their pyridinium residues and the chromophore closed by a bridge group, as a result of the electronic asymmetry of the dye molecules. Two signals of the β-protons of the pyrylium residue are also observed in the PMR spectrum of the thiapyrylocarbocyanine with structure III (δ 6.65 and 7.25 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 dyes synthesized. From a comparison of these values with the corresponding characteristics for analogous trimethinecyanines with an unclosed chromophore (thiapyrylocarbocyanine IIIa, thiapyridocarbocyanine IVa [7], and pyrylopyridocarbocyanine VIIa [5]), it follows that, like the symmetrical trimethinecyanines [1], in trimethinecyanines constructed from heteroresidues differing in electron-donor capacity, the cyclic groups cause a deepening of the color, and in this case the ethylene group has a greater effect than the trimethylene group. Similarly to the symmetrical pyrylocarbocyanines [1], the introduction of an ethylene bridge into the asymmetrical pyrylopyridocarbocyanine VII is accompanied by an increase

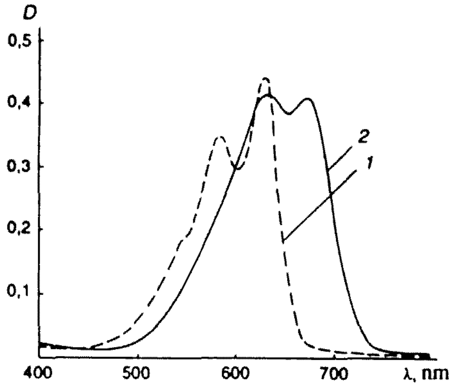
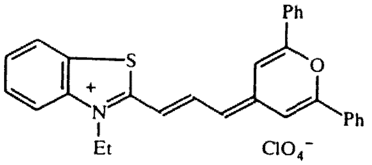


Fig. 1. Absorption spectra in CH_2Cl_2: 1) thiapyrylocarbocyanine XI; 2) its analog III ($C \sim 5.2 \cdot 10^{-6}$ g/liter).

in the intensity of the absorption bands, whereas the introduction of a trimethylene group is accompanied by a drop in it, associated with the appearance of steric hindrances in the molecule. However, it should be emphasized that although the qualitative similarity in the influence of the bridge groups on the shift of the absorption bands and the change in their intensity is preserved in the series of symmetrical and asymmetrical carbocyanines, quantitatively the effect should be different. This is manifested in a certain increase in the deviation of the dyes VII, VIII, and III under the influence of the bridge groups, calculated both according to the values of λ_{max} (which is more rigorous) and according to the first moments of the bands ($D_{\lambda max}$ and D_M, Table 1), in comparison with the values of the deviation for their analogs with an open polymethine chain ($D_{\lambda max}$ and D_M for the analogs VII (or VIII) and III, correspondingly equal to 87, 77.2, 0.5, and 18.7) [7]. The change in the values of the deviation may be due to a change in the asymmetry of the dyes under the influence of the electronic effect of the bridge groups (primarily ethylene) or steric hindrances to a coplanar arrangement of the molecule caused by them. Since the order of the bond of the chromophore adjacent to the more electron-donor heterocyclic residue is lowered in asymmetrical carbocyanine molecules, under the influence of steric hindrances caused by the bridge, the indicated heteroresidue can be rotated through a greater torsional angle to the remainder of the molecule than in the corresponding symmetrical dye. The latter factor, in particular, is probably responsible for the greater increase in the values of the deviation under the influence of a trimethylene bridge than of an ethylene bridge (the dyes VII and VIII). The assumption of an increase in the electronic asymmetry of trimethinecyanines with an asymmetrical structure under the influence of the hydrocarbon bridge groups is supported by a comparison of the shape of the absorption curve of the dye III and its analog with an open chromophore XI [7] (Fig. 1). It is known that with increasing asymmetry of the polymethine dyes, the probability of transitions to vibrational sublevels increases [8]. As can be seen from Fig. 1, in the dye XI (curve 1) the transition without a change in the vibrational quantum number is more intense, whereas in the dye III (curve 2), on the contrary, the transition with a change is more intense.



XI

In contrast to the examples cited for thiapyridocarbocyanines, the introduction of an ethylene bridge (the dye IV) causes not an increase but a drop in the value of the deviation calculated both according to the absorption maximum and according to the first moment of the bands ($\Delta D_{\lambda max} = -5$ nm; $\Delta D_M = -7.4$ nm), i.e., in the molecule of IV the order of the bond around which rotation between the enzothiazole residue and the chromophore occurs is not lower than 1.5 (as in III) but higher.

TABLE 1. Characteristics of the Compounds Synthesized

Compound	Gross formula	T_m, °C	Electronic spectrum, λ_{max}, nm, log (ε) (CH_2Cl_2)	$D\lambda$, nm	M^{-1}, nm	D_M, nm	PMR spectrum, δ, ppm (CD_3CN)†	Yield, %
III*	$C_{31}H_{26}ClNO_5S$	Above 256	630 (4,898), 673 (4,889)	12,0	624,3	41,7	1.46 (3H, t, CH_3), 2.76 (2H, m, CH_2 ring), 2.96 (2H, m, CH_2 ring), 4.51 (2H, q, CH_2), 6.65 (1H, d, β-H pyryl. ring), 7.25 (1H, d, β'-H pyryl. ring), 7.29....7.88 (14H, m, Ar-H), 7.90 (1H, s, meso-H)	62
IV*	$C_{32}H_{29}ClN_2O_4S$	140...141	652 (4,870)	14,0	633,2	6,7	1.29 (3H, t, CH_3), 2.77 (4H, m, CH_2), 3.34 (3H, s, CH_3), 4.16 (2H, q, CH_2), 7.00...7.31 (6H, m, Ar-H), 7.56 (10H, m, Ar-H), 7.73 (H, s, meso-H)	67
VII*	$C_{40}H_{31}ClNO_5$	195...196	644 (4,847)	96,0	616,5	92,0	1.72 (4H, m, CH_2), 3.46 (3H, s, CH_3), 6.46 (H, d, β-H pyryl. ring), 6.98 (H, d, β'-H pyryl. ring), 7.35 (6H, m, Ar-H), 7.42 (2H, s, β-H pyrid. ring), 7.59 (10H, m, Ar-H), 7.75 (4H, m, Ar-H), 7.86 (H, s, meso-H)	89
VIII	$C_{41}H_{33}ClNO_5$	198...200	607 (4,395)	101,5	589,0	94,6	10) 2.01 (2H, m, CH_2 centr.), 2.48 (4H, m, CH_2), 3.48 (3H, s, CH_3), 6.82 (H, d, β-H pyryl ring), 7.21 (H, d, β'-H pyryl. ring), 7.40 (7H, m, Ar-H), 760 (9H, m, Ar-H), 7.77 (2H, s, β-H pyrid. ring), 7.83 (4H, m, Ar-H), 7.92 (H, s, meso-H)	88
IX	$C_{41}H_{35}ClN_2O_4$	173...174	721 (5,092)	–	682,4	–	2.78 (4H, m, CH_2), 3.48 (6H, s, CH_3), 6.51 (2H, d, β-H ring), 7.05 (2H, d, β'-H ring), 7.38-7.60 (17H, m, Ar-H), 7.78-7.90 (3H, m, Ar-H), 7.93 (H, s, meso-H)	85
X	$C_{42}H_{37}ClN_2O_4$	158...160	687 (4,984)	–	660,9	–	1.98 (2H, m, CH_2 centr.), 2.55 (4H, m, CH_2), 3.65 (6H, s, CH_3), 6.75 (2H, d, β-H ring), 6.98 (2H, d, β'-H ring), 7.47 (4H, m, Ar-H), 7.58 (12H, m, Ar-H), 7.92 (4H, m, Ar-H), 7.93 (H, s, meso-H)13)	89

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*For analogs unsubstituted in the chain: λ_{max} 588, 625, log ε 4.91, 5.00; IVa) λ_{max} 585, log ε 5.10; VIIa) λ_{max} 578, log ε 4.81.

†The ppm values were determined according to the center of the multiplets.

TABLE 2. Electronic Spectra of Carbocyanines V-X in Trifluoroacetic Acid*

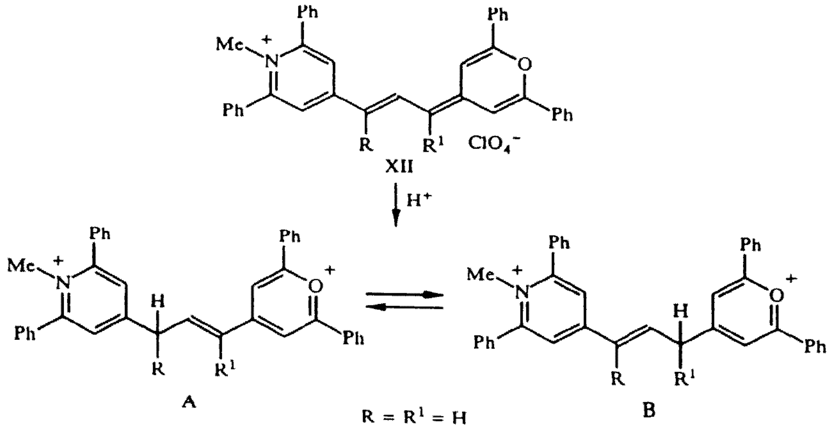
Compound	λ_{max}, nm*	lg ε
III	282, 352, 429	4,340, 4,442, 3,291
IV	296, 425	4,449, 3,765
V	282, 358, 414	4,551, 4,548, 4,703
VI	281, 353, 412	4,546, 4,583, 4,679
VII	301, 410	4,604, 4,509
VIII	299, 407	4,434, 4,299
IX	304, 407	4,624, 4,090
X	297	4,349

*Electronic spectra in trifluoroacetic acid of the cations: 2,6-diphenyl-4-methylpyrylium) λ_{max} 278, 401, log ε 4.211, 4.401; 1,4-dimethyl-2,6-diphenylpyridinium) λ_{max} 298, log ε 4.135; 2-methyl-3-ethylbenzothiazolium) λ_{max} 277, log ε 4.006.

TABLE 3. Data of Elementary Analysis of the Compounds Synthesized

Compound	Found, %				Calculated, %			
	C	H	N (S)	Cl	C	H	N (S)	Cl
II	—	—	(6,51)	13,91	—	—	(6,22)	13,86
III	—	—	3,85	5,43	—	—	4,19	5,13
IV	75,14	5,09	—	5,54	75,16	5,08	—	5,40
VII	74,90	4,89	—	5,61	74,90	4,87	—	5,50
VIII	—	—	4,87	5,72	—	—	4,89	6,19
IX	—	—	4,21	5,25	—	—	4,28	5,40
X	—	—	(5,96)	6,41	—	—	(5,71)	6,34

All of the asymmetrical pyrylocyanines synthesized, when dissolved in trifluoroacetic acid, are protonated with the formation of dications, analogously to the symmetrical pyrylocyanines, both containing cyclic groups [1] and without them [9]; in the case under consideration, as a result of protonation at different α-positions of the chromophore, two types of dications can be formed:



From the spectral data presented in Table 2 it is evident that in the spectra of dications formed from dyes of the type of VII and VIII bands characteristic of the 1,4-dimethyl-2,6-diphenylpyridinium cation (λ_{max} = 298 nm, log ε = 4.135) and bands in the region of ~410 nm, analogous to those contained in the spectra of the dications formed in the protonation of symmetrical pyrylocyanines V and VI, are observed and correspond to the 4-cycloalkenyl-2,6-diphenylpyrylium fragment. Consequently, the indicated dyes are protonated primarily with the formation of dications of the A type as a result of the addition of a proton to the α-position of the chromophore next to the more electron-donor pyridinium residue. Calculation of the model system XII, performed in the PPP approximation with the parameters for the atoms and bond lengths taken from [10], showed that the formation of a type A dication from it is accompanied by a smaller loss of total π-energy (E_π) than the formation of a B-type dication. The calculation led to the following values for the total π-electron energy for the ground state of the cation XII and the two subsystems A and B with a localized carbon atom in one of the α-positions of the chromophore: $E_\pi = -2273.42$ eV, $E_{\pi A} = 2159.94$ eV, $E_{\pi B} = -2159.81$ eV. Thus, the energy loss in the protonation of the cation XII with the formation of the dication A ($\Delta E_\pi = 113.48$ eV) is 0.13 eV less than for the dication B ($\Delta E_\pi = 113.61$ eV). Calculation for the dye III leads to an analogous result: its protonation at the α-position of the chromophore next to the more electron-donor benzothiazole residue is also accompanied by a smaller loss of π-electronic energy of the system.

EXPERIMENTAL

The electronic absorption spectra of compounds III, IV, VII-XI were measured on a Specord M-400 spectrophotometer. The PMR spectra were measured on a Bruker WP-200 spectrometer 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. The eluent was acetonitrile.

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

The compounds were crystallized: II) from a mixture of ethanol with water (14:1); III) from acetonitrile; VII, VIII, X) from absolute methanol.

2-(2-Morpholinocyclopentyl)-3-ethylbenzothiazolium Diperchlorate (II). 2-(2-Morpholinocyclopent-1-enyl)-benzothiazolium perchlorate (2.6 g, 6.25 mmoles), produced analogously to [4], was dissolved with mixing in 50 ml of absolute ether. Then 0.25 g (6.63 mmoles) sodium borohydride was added to the solution and mixed for 30 min. When the reaction mixture cooled, 2.5 ml of acetic acid was slowly added dropwise to it, and after 5 min, 1.5 ml of 57% perchloric acid was added. The mixture was mixed for another 1 h and poured out into absolute ether. The salt obtained was filtered off and washed with ether. Yield 0.9 g (28%). $C_{17}H_{24}Cl_2N_2N_2O_9S$. mp 164-166°C.

2-[3-(2,6-Diphenylpyranylidene-4)-1,3-dimethylenepropen-1-yl-1]-3-ethylbenzylthiazolium Perchlorate (III). A mixture of 0.3 g (0.59 mmole) of the benzothiazolium diperchlorate II, 0.114 g (0.29 mmole) of 2,6-diphenyl-4-ethylmercaptopyrylium perchlorate, and 0.05 g anhydrous sodium acetate in 1 ml of acetic anhydride was heated to boiling for 2 min. The dye was filtered off and washed with ether.

The characteristics of the compounds obtained are given in Table 1.

2-[3-(2,6-Diphenylpyridinylidene-4)-1,3-dimethylpropen-1-yl-1]-3-ethylbenzylthiazolium Perchlorate (IV). A mixture of 0.1 g (0.19 mmole) of the carbocyanine III, 0.5 ml of a 7% methanol solution of methylamine, and 5 ml DMFA was exposed at room temperature for 45 min. The dye was precipitated with an aqueous solution of sodium perchlorate, filtered off, and washed with water and with ether.

1-Methyl-2,6-diphenyl-4-[3-(2,6-diphenylpyranylidene-4)-1,3-dimethylpropen-1-yl-1]pyridinium perchlorate (VII) and 1-methyl-2,6-diphenyl-4-[3-(2,6-diphenylpyranylidene-4)-1,3-trimethylpropen-1-yl-1]pyridinium perchlorate (VIII) were produced analogously to IV from pyrylocarbocyanines V and VI, respectively.

1-Methyl-2,6-diphenyl-4-[3-(1-methyl-2,6-diphenylpyridinylidene-4)-1,3-dimethylpropen-1-yl-1]pyridinium Perchlorate (IX). A mixture of 0.2 g (0.32 mmole) of the carbocyanine V and 2 ml of a 7% methanol solution of methylamine in 5 ml of dimethyl sulfoxide was heated at 70°C for 9 min. It was treated analogously to IV.

1-Methyl-2,6-diphenyl-4-[3-(1-methyl-2,6-diphenylpyridinylidene-4)-1,3-timethylenepropen-1-yl-1]pyridinium perchlorate (X) was produced from the pyrylocyanine VI analogously to IX in 30 min.

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