PYRYLOCYANINES. 10.* ISOBENZOTHIOPYRYLOCYANINES

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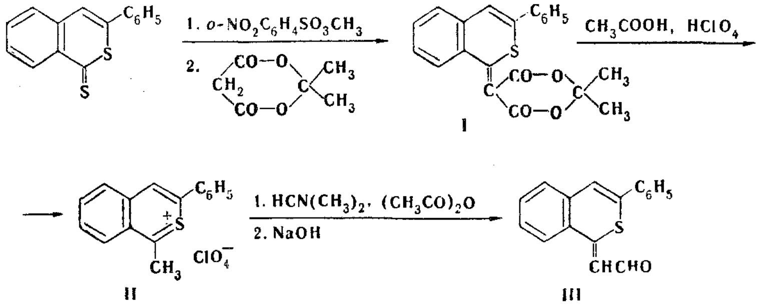
UDC 547.818.3:541.651:668.819.45

Polymethine dyes with symmetrical and unsymmetrical structures and 3-phenyl-2-benzothiopyrylium derivatives were synthesized. The color of these dyes is discussed.

In order to compare the colors of monotypically constructed dyes, the chromophore system in which terminates with oxygen or sulfur atoms, in the present research we obtained sulfur-containing analogs of 3-phenyl-2-benzopyrylium derivatives [1], viz., isobenzothiopyrylocyanines. For their synthesis we started from 1-methyl-3-phenyl-2-benzothiopyrylium perchlorate (II) or 1-formylmethylene-3-phenyl-2-benzothiopyran (III). Perchlorate II was obtained by acid cleavage of I, the product of condensation of 2,2-dimethyl-4,6-dioxo-1,3-dioxane with 1-(methylthio)-3-phenyl-2-benzothiopyrylium o-nitrobenzenesulfonate; the latter was synthesized by the addition of methyl o-nitrobenzenesulfonate to 3-phenyl-2-benzothiopyran-1-thione. Aldehyde III was obtained by saponification with aqueous alkali of the product of condensation of salt II with dimethylformamide (DMF).



Dye IV was obtained by condensation of isobenzothiopyrylium salt II with p-dimethylaminobenzaldehyde in acetic anhydride, while symmetrical and unsymmetrical monomethylidynecyanines Va and VIa were obtained by reaction in the same solvent with 3-phenyldithioisocoumarine or 1-thioflavone, respectively. Unsymmetrical monomethylidynecyanine VII was synthesized from the oxygen analog of salt II and base I. Symmetrical isobenzothiopyrylotrimethylidynecyanine Vb was obtained in the same way as its oxygen-containing analog by stepwise condensation of 2 moles of salt II with ethyl N-phenylformimidate, while unsymmetrical trimethylidynecyanines VIb, VIII, and IX were obtained by reaction of aldehyde III with 4-methyl-1-thioflavylium, 1,2,3,3-tetramethyl(3H)indolium, and 2,3-dimethylbenzothiazolium salts.

Symmetrical isobenzothiopyrylocyanines behave like isobenzopyrylocyanines in organic solvents, i.e., their alcohol solutions are relatively unstable. Dissolving in trifluoroacetic acid is accompanied by protonation, and monomethylidyne Va is protonated more readily than its oxygen-containing analog, although the addition of perchloric acid is required for complete conversion to the dication in this case also. The absorption spectrum of the product of protonation of Va is similar to the absorption spectrum of salt II, which confirms the structure of the starting monomethylidynecyanine.

A comparison of the long-wave bands in the electronic absorption spectra of solutions of unsymmetrical carbocyanines VIII and IX (Fig. 1) shows that the probability of transition to vibrational sublevels, as in series of other pyrylocyanines (see [1]), increases as the electronic asymmetry of the dyes increases on passing from VIII to IX. Judging from the

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*See [1] for communication No. 9.

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Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 777-782, June, 1980. Original article submitted August 6, 1979.

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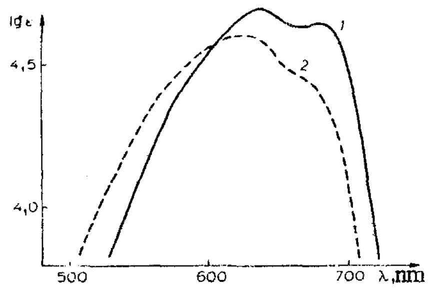
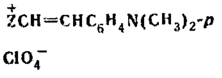
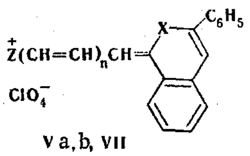


Fig. 1. Absorption spectra in methylene chloride: 1) carbocyanine VIII; 2) carbocyanine IX.

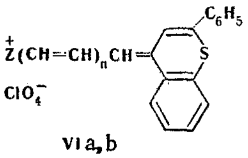


$\overset{+}{Z}CH{=}CHC_6H_4N(CH_3)_2\text{-}p$ ClO_4^-

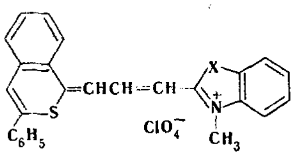
IV



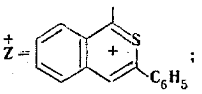
V a, b, VII



VI a, b



VIII, IX



; V, IX X–S;
VII X=O; VIII X=C(CH$_3$)$_2$;
V a, VI a, VII n=0; Vb, VI b n=1

greater intensity of the vibrational transitions in the case of dyes VIII and IX as compared with their oxygen-containing analogs, it may be assumed that the isobenzothiopyrylium ring has a smaller degree of electron-donor character than the isobenzopyrylium ring. The absorption curve of trimethylidynecyanine VIb, which contains a thioflavylium residue, has, like isobenzothiopyrylotrimethylidynecyanine Vb, the form that is usually observed for polymethine dyes, and this indicates the relatively small difference in the electron-donor character of the 3-phenylisobenzothiopyrylium and thioflavylium rings.

The characteristics of the long-wave absorption bands of the dyes obtained and the average positions (M^{-1}) are presented in Table 1. The deviations (D_M), which were calculated from the average positions of the band and used, as in other cases [1], to estimate the electron-donor character (the relative "basicity") of the sulfur-containing heterocycle under examination, are also presented for unsymmetrical trimethylidynecyanines. The λ_{max}, M^{-1}, and D_M values for the analogous thioflavylocyanines (the first numbers) and isobenzopyrylocyanines (the second numbers) are presented in parentheses for comparison.

In [1] it was shown that symmetrical mono- and trimethylidyneisobenzopyrylocyanines absorb ~10 nm higher than their flavylium analogs. Monomethylidynecyanine Va also absorbs higher than thioflavylomonomethylidynecyanine; however, the difference in the positions of the absorption maxima reaches 85 nm. On the other hand, the absorption maximum of trimethylidynecyanine Vb is shifted 20 nm to the long-wave side as compared with the absorption maximum of its thioflavylium analog. A bathochromic shift, although it is smaller, is also retained between the M^{-1} values for these compounds. Owing to this, the vinylene shift between the absorption bands of dyes Va, b reaches an unusually large value ($\Delta\lambda$ = 205 nm, ΔM^{-1} = 179 nm). It follows from Table 1 that the vinylene shift in the case of oxygen-containing analogs of the dyes under consideration and in the case of the isomeric thioflavylocyanines is close to the shift (100 nm) characteristic for symmetrical polymethine dyes. The anomalously large vinylene shift for dyes Va, b is due mainly to the relatively intense color of monomethylidynecyanine Va, which can be explained by electronic interaction through space between the sulfur atoms of the heterocyclic residues. This interaction is drawn upon to explain the somewhat increased value of the analogous shift in series of polymethine dyes constructed from other sulfur-containing heterocycles (for example, thiacyanines [2, 3]). However, in the described cases the exceeding of the first vinylene shift is considerably smaller. It is often comparable to the value observed in certain cases in which interaction

TABLE 1. Characteristics of the Long-Wave Absorption Bands of Solutions of Isobenzothiopyrylocyanines[a] in Methylene Chloride

Compound	λ_{max}, nm	lg ε	M^{-1}, nm	D_M, nm
IV	740 (—; 678)	5,03	696.9 (—; 645.1)	—2,8b (—; —7.7 b)
Va	615 (700; 596)	4,75	609.3 (686,9; 563)	—
Vb	820 (800; 707)	5.01	788,1 (779,6; 674,7)	—
VIa	676	4,70	671,0	
VIb	810	5,11	782.4	1,4 (—; 0.4)
VII	604	4,70	587,4	
VIII	636, 680 (633, 676; 582, 626)	4,70 4,65	624,5 (624,5; 579,7)	32,6 (28.3; 20,6)
IX	617 (617; 574, 616)	4,60	601.7 (603,2; 568.6)	64.3 (58,5; 40,6)

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[a] The characteristics of the analogous thioflavylocyanines and isobenzopyrylocyanines are presented in parentheses.

[b] The M^{-1} value for Michler's hydrol (600 nm) was used for the calculation.

between the nonbonded sulfur atoms is altogether impossible with respect to the structural features. For example, in the thiacyanine series, in which interaction is possible, and in the 2,6-diphenylthiopyrylo-4-cyanine series, in which it is impossible, the first vinylene shifts determined from the absorption maxima virtually coincide (they are, respectively, 132 and 130 nm) [2]. The considerably greater (as compared with the previously observed value) vinylene shift in the case under consideration makes it possible to propose that the effect from the electronic interaction of the nonbonded sulfur atoms increases if these atoms bear a positive charge.

The fact that the absorption band of unsymmetrical monomethylidynecyanine VIa (M^{-1} = 671 nm) is considerably closer to the absorption band of the symmetrical thioflavylomonomethylidyne cyanine (M^{-1} = 686.9 nm) than to that of the symmetrical isobenzothiopyrylomonomethylidynecyanine (M^{-1} = 609.3 nm) can be explained by the same reason. The reverse dependence is more likely observed in a series of oxygen-containing analogs of these dyes. The anomalously high degree of absorption of monomethylidynecyanine Va is also responsible for the fact that the deviation of styryl IV calculated with allowance for its M^{-1} value and the analogous characteristic of a vinylog of Michler's hydrol (690.2 nm) has a negative value (—47.2 nm) that is considerably larger in absolute value than the value calculated from the M^{-1} values of carbocyanine Vb and Michler's hydrol (Table 1). The deviations calculated by these two methods for the dimethylaminostyryl derivative of the 3-phenylisobenzopyrylium ion differ to a considerably lesser extent (they are —18.5 and —7.7 nm, respectively). However, the marked dependence of the absorption on the electronic interaction through space of the sulfur atoms that bear a positive charge need to be verified for other compounds and require theoretical substantiation. In fact, it is not clear why, for example, the moment of the absorption band of unsymmetrical monomethylidynecyanine VII, which contains 3-phenylisobenzopyrylium and 3-phenylisobenzothiopyrylium residues, virtually coincides with the average of the moments of the bands of symmetrical monomethylidynecyanines constructed from the same heterocycles.

During an examination of the characteristics of the unsymmetrical carbocyanines it is apparent that a deviation is actually absent in the case of dye VIb, which is made up of isobenzothiopyrylium and thioflavylium residues, and this indicates the similar electron-donor character of these heterocycles. In contrast to carbocyanine VIb, significant deviations, which are higher than for the analogous dyes that contain 3-phenylisobenzopyrylium residues, are observed for dyes VIII and IX. The latter indicates that in this case, as in a number of others, sulfur-containing heterocycles have greater "basicities" (electron-donor character) than their oxygen-containing analogs. The deviations of dyes VIII and IX are somewhat greater than those of similar thioflavylocyanines, and this makes it possible to assume that in the dye molecules the "basicity" of the heterocycle under consideration is somewhat lower than that of the thioflavylidene residue. The opposite trend is observed for the oxygen-containing analogs of these dyes. However, the noted effects are not large enough in both cases to draw rigorous conclusions.

TABLE 2. Characteristics of the Synthesized Compounds

Compound	mp, °C	Found, %		Empirical formula	Calc., %		Yield, %
		Cl	S		Cl	S	
I	246,5	—	8,9	$C_{21}H_{16}O_4S$	—	8,8	49
II	196	10,5	9,3	$C_{16}H_{13}ClO_4S$	10,5	9,5	80
III	106[a]	—	12,1	$C_{17}H_{12}OS$	—	12,1	89
IV	221[b]	7,2	—	$C_{25}H_{22}ClNO_4S$[c]	7,6	—	91
Va	288[d]	6,2	11,3	$C_{31}H_{21}ClO_4S_2$	6,4	11,5	65
Vb	257,5[b]	6,2	10,9	$C_{33}H_{23}ClO_4S_2$	6,1	11,0	63
VIa	262[b]	6,4	11,5	$C_{31}H_{21}ClO_4S_2$	6,4	11,5	60
VIb	248—249[b]	6,0	10,9	$C_{33}H_{23}ClO_4S_2$	6,1	11,0	94
VII	268[d]	6,6	6,1	$C_{31}H_{21}ClO_5S$	6,6	5,9	60
VIII	206[e]	6,7	6,2	$C_{29}H_{26}ClNO_4S$	6,8	6,2	46
IX	245[f]	7,0	12,4	$C_{26}H_{20}ClNO_4S_2$	7,0	12,6	66

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[a] From alcohol with water (3:1). [b] From acetonitrile. [c] Found %: C 64.2; H 4.4. Calculated %: C 64.2; H 4.7. [d] From acetic anhydride. [e] From acetic acid. [f] From acetic anhydride—acetic acid (1:2).

EXPERIMENTAL

The electronic absorption spectra of solutions ($8 \cdot 10^{-6}$ to $2 \cdot 10^{-5}$ mole/liter) of the compounds were recorded with an SF-4A spectrophotometer at layer thicknesses of 1 and 5 cm and were processed by means of the program presented in [1]. The PMR spectra of 0.1 M solutions of the compounds in CF_3CO_2H were determined with a Tesla BS-487 B spectrometer (80 MHz) at 20°C with tetramethylsilane as the internal standard. The purity of the preparations was monitored by thin-layer chromatography on Silufol UV_{254} plates (elution with acetonitrile).

1-(2,2-Dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)-3-phenyl-2-benzothiopyran (I). 3-Phenyl-2-benzothiopyran-1-thione was obtained by conversion of o-phenacylbenzoic acid [4] to the methyl ester [5] and treatment of the latter with phosphorus pentasulfide [5]. The product was freed of 3-phenyl-2-benzopyran-1-thione by conversion of the latter to o-phenacylbenzamide by heating with piperidine in absolute alcohol [6]. The benzothiopyranthione was heated at 100°C with methyl o-nitrobenzenesulfonate for 1 h, and a mixture of 4.5 g (10 mmole) of the resulting 1-(methylthio)-3-phenyl-2-benzothiopyrylium o-nitrobenzenesulfonate, 4.5 g (30 mmole) of 2,2-dimethyl-4,6-dioxo-1,3-dioxane, and 4.5 ml (32 mmole) of triethylamine was heated in 90 ml of absolute alcohol at 60-70°C for 2 h. The precipitate was removed by filtration and washed with alcohol (Table 2).

1-Methyl-3-phenyl-2-benzothiopyrylium Perchlorate (II). A 1.15-g (3 mmole) sample of thiopyran I was heated in a mixture of 20 ml of glacial acetic acid and 2.5 ml of 42% perchloric acid for 15 min on a boiling-water bath, after which the bulk of the acetic acid was removed by vacuum distillation (20-40 mm), and salt II was precipitated with ether, removed by filtration, and washed with acetic acid and ether. UV spectrum in trifluoroacetic acid, λ_{max} (log ε): 278 (4.63), 316 (3.80), and 424 nm (3.39). PMR spectrum: 3.72 (3H, s, CH_3); 8.8 and 7.67 (9H, m, benzene ring protons); 9.15 ppm (1H, s, 4-H).

1-Formylmethylene-3-phenyl-2-benzothiopyran (III). A solution of 0.675 g (2.0 mmole) of salt II and 2 ml (26 mmole) of DMF in 10 ml of acetic anhydride was heated to the boiling point, after which it was cooled, and the precipitated 1-(2-dimethylaminovinyl)-3-phenyl-2-benzothiopyrylium perchlorate was removed by filtration and dissolved in 30 ml of acetonitrile. The solution was shaken with 40 ml of a 2% aqueous solution of sodium hydroxide at room temperature for 30 min, and the precipitated III was removed by filtration.

1-(p-Dimethylaminostyryl)-2-benzothiopyrylium Perchlorate (IV). A solution of 0.084 g (0.25 mmole) of salt II and 0.045 g (0.30 mmole) of p-dimethylaminobenzaldehyde in 1 ml of acetic anhydride was refluxed for 5 min, after which the dye was removed by filtration and washed with acetic acid and ether.

1-[(3-Phenyl-2-benzothiopyran-1-ylidene)methyl]-3-phenyl-2-benzothiopyrylium Perchlorate (Va). This compound was obtained by refluxing a solution of 0.112 g (0.33 mmole) of salt II and 0.085 g (0.33 mmole) of 3-phenyl-2-benzothiopyran-1-thione in 2.5 ml of acetic anhydride for 2 min. UV spectrum in trifluoroacetic acid containing one drop of 40% $HClO_4$, λ_{max} (log ε): 286 (4.89), 322 (4.10), and 450 nm (4.14).

1-[3-(3-Phenyl-2-benzothiopyran-1-ylidene)prop-1-en-1-yl]-3-phenyl-2-benzothiopyrylium Perchlorate (Vb). A solution of 0.136 g (0.4 mmole) of salt II and 0.06 g (0.4 mmole) of ethyl N-phenylformimidate in a mixture of 2.4 ml of acetic anhydride and 1.6 ml of glacial acetic acid was refluxed for 2 min, after which it was cooled and treated with another 0.136 g of salt II and 0.04 g of anhydrous sodium acetate and again heated to the boiling point. The dye was removed by filtration and washed with acetic acid and ether.

1-[(2-Phenyl-1-benzothiopyran-4-ylidene)methyl]-3-phenyl-2-benzothiopyrylium Perchlorate (VIa). This compound was obtained from 1.11 g (0.33 mmole) of salt II and 1.05 g (0.44 mmole) of 1-thioflavone in 1 ml of acetic anhydride as in the preparation of IV.

1-[3-(2-Phenyl-1-benzothiopyran-4-ylidene)prop-1-en-1-yl]-3-phenyl-2-benzothiopyrylium Perchlorate (VIb). This compound was obtained from 0.104 g (0.4 mmole) of 1-formylmethylene-3-phenyl-2-bezothiopyran (III) and 0.136 g (0.4 mmole) of 4-methyl-1-thioflavylium perchlorate in 2 ml of acetic anhydride as in the preparation of IV.

1-[3-Phenyl-2-benzopyran-1-ylidene)methyl]-3-phenyl-2-benzothiopyrylium Perchlorate (VII). A solution of 0.194 g (0.6 mmole) of 1-methyl-3-phenyl-2-benzopyrylium perchlorate and 0.14 g (0.6 mmole) of 3-phenyl-2-benzothiopyran-1-thione in 2 ml of acetic anhydride was refluxed for 2 min.

1,3,3-Trimethyl-2-[3-(3-phenyl-2-benzothiopyran-1-ylidene)prop-1-en-1-yl]-3H-indolium Perchlorate (VIII). This compound was obtained from 0.156 g (0.6 mmole) of aldehyde III, 0.164 g (0.6 mmole) of 1,2,3,3-tetramethyl-3H-indolium perchlorate, and 0.05 g of anhydrous sodium acetate in a mixture of 3 ml of acetic anhydride and 2 ml of acetic acid by refluxing for 5 min. The product was isolated as in the preparation of IV.

2-[3-(3-Phenyl-2-benzothiopyran-1-ylidene)prop-1-en-1-yl]-3-methylbenzothiazolium Perchlorate (IX). This compound was obtained from 0.156 g (0.6 mmole) of aldehyde III and 0.165 g (0.6 mmole) of 2,3-dimethylbenzothiazolium methylsulfate by heating in the presence of 0.05 g of anhydrous sodium acetate in 4 ml of a mixture (1:1) of acetic acid with acetic anhydride. The dye was precipitated with ether and converted to the perchlorate by the addition of a solution of sodium perchlorate to a solution of the dye in glacial acetic acid.

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