PYRYLOCYANINES

VII.* XANTHYLO-, THIOXANTHYLO-, AND SELENOXANTHYLOCYANINES

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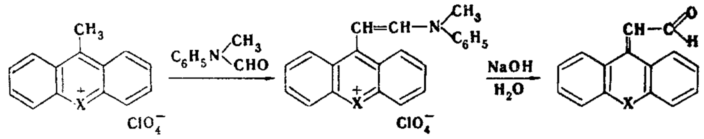
Trimethinecyanines with symmetrical and unsymmetrical structures containing xanthylium, thioxanthylium, and selenoxanthylium residues were synthesized. It was shown by the method of deviations that the "basicities" of the residues of the investigated three-ring heterocycles in the dyes change in the order O > S > Se. In series of 2,6-diphenyl-substituted 4-pyrylo-, 4-thiopyrylo-, and 4-selenopyrylotrimethinecyanines replacement of the phenyl substituents by annelated benzene rings affects the color to a considerably lesser degree than analogous replacement in 4-pyridocyanines.

Data on xanthylocyanines are limited [2, 3], only one thioxanthylocyanine dye has been described [3], and selenoxanthylocyanines have not been studied at all. The synthesis and spectroscopic investigation of dyes of this type constitute the subject of the present paper. The preparation of thio- and selenoxanthylocyanines is fraught with a number of difficulties caused by the low reactivities of 9-methylthioxanthylium and 9-methylselenoxanthylium salts (Ib, c). We were unable to synthesize symmetrical thioxanthylocyanine VI by condensation of salt Ib with ethyl orthoformate via a method similar to that used to prepare xanthylotrimethinecyanine V [2]. A number of thio- and selenoxanthylocyanines were obtained from 9-formylmethylenethioxanthene (IIIb) and its selenium analog (IIIc), which was synthesized by the method used to prepare 9-formylmethylenexanthene (IIIa) [2] via the scheme



I a-c† IIa-c IIIa-c

I-III a X=O; b X=S; c X=Se

Bis(9-thioxanthylo)trimethinecyanine perchlorate (VI) (Table 1) was obtained by condensation of aldehyde IIIb with thioxanthylium salt IIb, whereas its selenium anlog (VII), which, however, we were unable to purify, was obtained from aldehyde IIIc and salt IIc. In addition to the previously described unsymmetrical xanthylocyanines VIII [2], IXa [3], XIa [2], and XIIa [2], in the present research we obtained (9-xanthylo)(2,6-diphenyl-4-pyrylo)trimethinecyanine Xa and a number of unsymmetrical thio- and selenoxanthylocyanines (Table 2).

From the graphical depiction of the cation of xanthylotrimethinecyanine V (Fig. 1), which was accomplished with allowance for the valence angles, covalent radii, and effective radii of the atoms [4], it is seen that there is steric hindrance in it. This steric hindrance should be retained not only in the S, Se, and NCH_3 analogs of this dye but also in all unsymmetrical trimethinecyanines containing residues of the three-ring heterocycles under consideration. The presence of steric hindrance is in agreement with the

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* See [1] for communication VI.

†λ_{max} (40% perchloric acid), nm: Ia 366, Ib 376, Ic 388.

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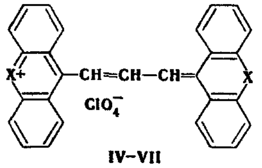
TABLE 1. Electronic Spectra of Symmetrical Trimethinecyanines



IV–VII

Compound	X	In CH_3NO_2			In CH_2Cl_2		
		λ_{max}, nm	$\varepsilon \cdot 10^{-4}$	M^{-1}, nm	λ_{max}, nm	$\varepsilon \cdot 10^{-4}$	M^{-1}, nm
IV	NCH_3	810 (723[3], 638)*	—	—	822	—	—
V	O	702 (708, 676)	8,0 (—, 24,4)*	679	714	10,2	687
VI	S	776 (796, 755)	3,0 (17,6; 21,8)	676	800	6,2	756
VII	Se	820 (835, 795)	— (13,4; 22,3)	—	—	—	—

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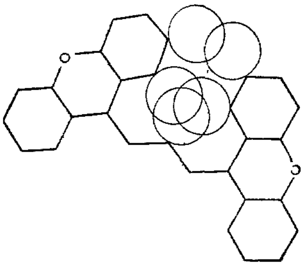
*The first number in parentheses is cited for 2-phenylquino trimethinecyanine and its O, S, and Se analogs, whereas the second number is cited for 2,6-diphenyl-4-pyridotrimethinecyanine and its O, S, and Se analogs.



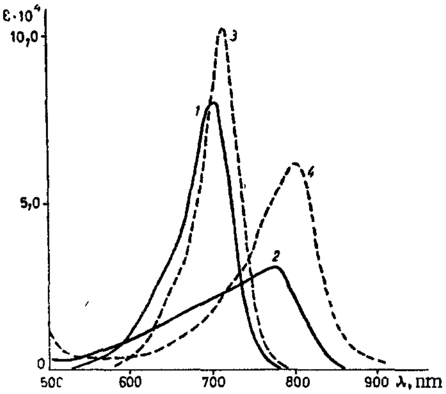


Fig. 1 Fig. 2

Fig. 1. Graphical depiction of the cation of bis(9-xanthylo)trimethinecyanine (V).

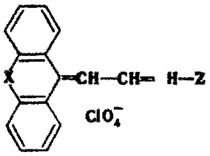
Fig. 2. Absorption spectra: 1) bis(9-xanthylo)trimethinecyanine (V) in CH_3NO_2; 2) in CH_2Cl_2; 3) bis(9-thioxanthylo)trimethinecyanine (VI) in CH_3NO_2; 4) VI in CH_2Cl_2.

low extinction of their long-wave absorption band. In addition to steric hindrance, the extremely low "basicities" of the heterocyclic systems under consideration also have a substantial effect on the absorption of these dyes. The absorption band of thioxanthylocyanine VI in nitromethane solution (Fig. 2) is considerably more diffuse and asymmetrical than the absorption band of xanthylocyanine V. The difference between the maximum of the band and its average position, determined by the ratio of the zero moment to the first moment (M^{-1}), for dye VI is 100 nm, whereas it is only 23 nm for dye V. This is probably associated with the fact that dye VI is constructed from less "basic" and more weakly solvated heterocyclic residues, owing to which the polymethine chromophore of VI takes onto itself a considerable fraction of positive charge and is therefore strongly solvated. The absorption bands in the spectra of a methylene chloride solution of the dye are less diffuse, whereas they are less asymmetrical in character for thioxanthylocyanine VI.

It is seen from a comparison of the λ_{max} values of the dyes in nitromethane and methylene chloride solutions presented in Tables 1 and 2 that the unsymmetrical dyes are considerably more solvatochromic than the symmetrical dyes. For example, a bathochromic shift of the long-wave absorption band of 65 nm is observed in the spectra of solutions of trimethinecyanines IXc and Xc when nitromethane is replaced by methylene chloride.

It is apparent from Table 1 that replacement of phenyl substituents in a number of symmetrical trimethinecyanines by annelated benzene rings affects the color in different ways, depending on the character of

TABLE 2. Electronic Spectra of Unsymmetrical Xanthylocyanines



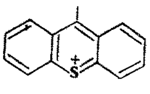
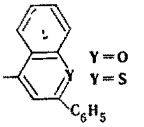
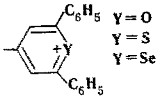
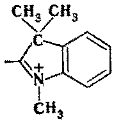
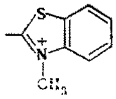
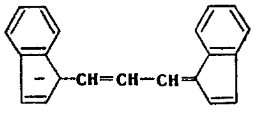
Compound	X	Z	In CH₃NO₂ λ_1, nm	$\varepsilon_1 \cdot 10^{-4}$	λ_2, nm	$\varepsilon_2 \cdot 10^{-4}$	M^{-1}, nm	D, nm	D_M, nm	In CH₂Cl₂ λ_1, nm	$\varepsilon_1 \cdot 10^{-4}$	λ_2, nm	$\varepsilon_2 \cdot 10^{-4}$	M^{-1}, nm	D, nm	D_M, nm
VIII	O		380	1,9	713	3,5	678	25	0	382	—	750	—	729	7	1
IXa	O		395	1,7	660	5,9	637	47	47	375	2,4	685	8,2	660	29	33
IXb	S		400	1,6	630	2,8	615	154	105	407	1,8	695	4,1	673	105	97
Xa	O		415	2,0	598	5,4	582	91	76	425	2,2	640	7,8	622	59	51
Xb	S		425	2,1	590	2,9	582	125	122	435	1,8	645	3,8	631	137	119
Xc	Se		415	2,0	630	2,9	601	~177	—	420	1,9	695	3,1	—	—	—
XIa	O		—	—	522	4,4	513	101	89	—	—	550	5,0	543	79	65
XIb	S		400	1,6	515	3,2	507	157	93	420	1,6	552	3,4	535	120	109
XIc	Se		410	2,0	500	2,1	—	~182	—	425	2,1	540	2,6	—	—	—
XIIa	O		—	—	500	3,9	485	132	114	—	—	530	4,1	521	109	95
XIIb	S		390	1,4	480	2,4	470	177	139	402	1,5	526	2,7	507	156	141
XIIc	Se		395	2,2	470	2,2	—	~219	—	408	2,0	514	1,9	—	—	—

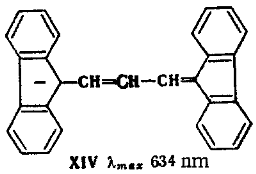
TABLE 3. Characteristics of the Synthesized Dyes

Compound	mp, °C (crystallization solvent)	Empirical formula	Found, %	Calc., %	Yield, %
IIb	160 (acetic acid)	$C_{22}H_{18}ClNO_4S$	S 7,7	S 7,8	94
IIIb	101 (alcohol)	$C_{15}H_{10}OS$	S 13,2	S 13,4	69
IIIc	143 (alcohol)	$C_{15}H_{10}OSe$	Se 27,6	Se 27,9	25
VI	173	$C_{29}H_{19}ClO_4S_2$	Cl 6,8; S 11,9	Cl 6,7; S 12,1	17
IXb	245 (acetic acid)	$C_{31}H_{21}ClO_4S_2$	Cl 6,3; S 11,2	Cl 6,4; S 11,5	75
Xa	298 (acetic anhydride + acetic acid)	$C_{33}H_{23}ClO_6$	Cl 6,4	Cl 6,4	68
Xb	165 (acetic acid)	$C_{33}H_{23}ClO_4S_2$	Cl 6,0; S 10,6	Cl 6,1; S 11,0	90
Xc	215	$C_{33}H_{23}ClO_4Se_2$	Cl 5,4; Se 23,6	Cl 5,3; Se 23,4	60
XIb	216 (alcohol + n-heptane 1 : 1)	$C_{27}H_{20}ClNO_4S$	Cl 7,3	Cl 7,2	87
XIc	198 (alcohol + n-heptane)	$C_{27}H_{20}ClNO_4Se$	Cl 6,9	Cl 6,6	78
XIIb	287 (acetic acid)	$C_{24}H_{18}ClNO_4S_2$	Cl 6,9; S 13,0	Cl 7,3; S 12,8	40
XIIc	280 (acetic acid)	$C_{24}H_{18}ClNO_4SSe$	Cl 6,7; Se 14,7	Cl 6,6; Se 14,9	49

heteroatom X. The successive transition from 2,6-diphenyl-4-pyrido- to 2-phenyl-4-quino- and then to 9-acridinotrimethinecyanine is accompanied by an approximately identical shift of the absorption maximum to the long-wave region (81 and 87 nm). In the analogous series of oxygen-, sulfur-, and selenium-containing dyes replacement of the first phenyl group is also accompanied by deepening of the color, but the observed effect is considerably smaller (32, 41, and 40 nm); however, replacement of the second phenyl group leads to a certain heightening of the color [hypsochromic shifts in the series of O, S and Se derivatives (6, 20, and 15 nm)] rather than to deepening of the color. This difference is due in part to the fact that the phenyl substituents in quaternary salts of the nitrogen heterocycles under consideration deviate from the plane of the heteroring because of steric hindrance [5]. However, one should note that annelation itself of the benzene rings in dyes of different types may be accompanied by different effects. Thus, whereas transition from unsubstituted 4-pyridocyanine to 4-quinocyanine is accompanied by pronounced deepening of the color (103 nm) [3], the transition from trimethinecyanine XIII to XIV induces a bathochromic shift of only 7 nm [6].



XIII λ_{max} 627 nm



XIV λ_{max} 634 nm

In addition to the long-wave absorption bands of all of the examined dyes at 400 nm, bands due to the adsorption of the heterocyclic rings are observed. The extinction of the first overtone of the polymethine dyes usually is of the order of 10^4 liter · $mole^{-1}/cm^{-1}$. The intensity of the short-wave maxima of the dyes under consideration is of the same order. However, whereas the intensity of the overtones is ~0.1 of the intensity of the primary transition for thiocarbocyanines, the intensity of the short-wave bands for the dyes obtained in this study approaches the intensity of the primary transition, and in the series of compounds (XIc, XIIc) the long- and short-wave bands overlap markedly.

The deviations (D) calculated from both the absorption maxima and by the method of moments, which is more rigorous for dyes with different forms of absorption curves [8], are presented in Table 2. It is apparent from the D_M values for xanthylotrimethinecyanine VIII that the xanthylium and thioxanthylium rings have close "basicities." However, a comparison of the deviations of dyes Xa-c, XIa-c, and XIIa-c shows that, like one- and two-ring heterocycles, the "basicities" of the three-ring heterocycles decrease in the order O > S > Se, depending on the heteroatom. However, the calculation of the deviations from the moments of the bands also leads to erroneous conclusions in a number of cases. For example, higher D_M values were obtained for thioxanthylothiopyrylotrimethinecyanine Xb, which has less electronic asymmetry, than for the more asymmetric thioxanthyloindotrimethinecyanine XIb. The latter is probably explained not only by the above-mentioned solvation effect but also by the restricted character of the method of deviations for markedly asymmetrical dyes [9].

EXPERIMENTAL METHOD

The electronic absorption spectra were recorded with an SF-4a spectrophotometer. The purity of the preparations was monitored by thin-layer chromatography (TLC). Chromatography was carried out on plates with a fixed layer of Silufol UV 254 silica gel. Nitromethane was used for elution of the products.

9-[ω-(N-Methylanilino)vinyl]thioxanthylium Perchlorate (IIb) and 9-[ω-(N-Methylanilino)vinyl]selenoxanthylium Perchlorate (IIc). These dyes were obtained by the reaction of 9-methylthioxanthylium perchlorate (Ib) [10] or 9-methylselenoxanthylium perchlorate (Ic) [11] with N-methylformanilide by the method used to prepare IIa [2] (Table 3).

9-Formylmethylenethioxanthene (IIIb). A 10% solution of NaOH was added dropwise with stirring to a solution of 2.9 g (7 mmole) of IIb in 200 ml of alcohol until the color of the solution changed to yellow. It was then diluted with water until it became turbid, after which it was allowed to stand. The precipitated product was removed by filtration and chromatographed from chloroform on aluminum oxide.

9-Formylmethyleneselenoxanthene (IIIc). The method used to prepare IIIb was used to obtain this compound from 2.4 g (5 mmole) of IIc in 100 ml of acetone.

Bis(9-thioxanthylo)trimethinecyanine Perchlorate (VI). A solution of 0.164 g (0.53 mmole) of Ib and 0.12 g (0.53 mmole) of IIIb in 2 ml of acetic anhydride was heated at 140° for 10 min. The precipitated dye was removed by filtration and washed successively with acetic acid, acetic anhydride, and benzene.

Bis(9-selenoxanthylo)trimethinecyanine Perchlorate (VII). As in the preceding experiment, this compound was obtained by condensation of Ic with IIIc.

(9-Thioxanthylo)(4-thioflavylo)trimethinecyanine Perchlorate (IXb). This compound was obtained by heating 0.168 g (0.5 mmole) of 4-methylthioflavylium perchlorate [12] with 0.12 g (0.5 mmole) of IIIb in 2 ml of acetic anhydride at 140° for 30 min.

(9-Xanthylo)(2,6-diphenyl-4-pyrylo)trimethinecyanine Perchlorate (X). This compound was obtained by heating 0.172 g (0.5 mmole) of 2,6-diphenyl-4-methylpyrylium perchlorate and 0.108 g (0.5 mmole) of 9-formylmethylenexanthene in 3 ml of acetic anhydride at 140° for 15 min.

(9-Thioxanthylo)(2,6-diphenyl-4-thiopyrylo)trimethinecyanine Perchlorate (Xb). The method used to prepare IXb was used to obtain this compound from 2,6-diphenyl-4-methylthiopyrylium perchlorate [13] and IIIb.

(9-Selenoxanthylo)(2,6-diphenyl-4-selenopyrylo)trimethinecyanine Perchlorate (Xc). This compound was obtained by heating 0.204 g (0.5 mmole) of 2,6-diphenyl-4-methylselenopyrylium perchlorate [14] and 0.142 g (0.5 mmole) of IIIc in 4 ml of acetic anhydride at 130° for 10 min. The precipitated dye was removed by filtration and washed successively with acetic acid, benzene, and ether.

(9-Thioxanthylo)(1,3,3-trimethyl-2-indo)trimethinecyanine Perchlorate (XIb). A mixture of 0.31 g (1 mmole) of Ia and 0.2 g (1 mmole) of 1,3,3-trimethyl-2-formylmethyleneindoline in 4 ml of acetic anhydride was heated at 130° for 30 min, after which it was cooled and a few drops of 42%perchloric acid were added. The precipitated dye was then removed by filtration.

(9-Selenoxanthylo)(1,3,3-trimethyl-2-indo)trimethinecyanine Perchlorate (XIc). As in the preceding experiment, this compound was obtained from Ic and 1,3,3-trimethyl-2-formylmethyleneindoline.

(9-Thioxanthylo)(3-methylthia)trimethinecyanine Perchlorate (XIIb). A solution of 0.14 g (0.25 mmole) of 2,3-dimethylbenzothiazolium methosulfate and 0.12 g (0.25 mmole) of IIIb in 3 ml of acetic anhydride was heated at 130° for 30 min. The dye was precipitated by the addition of ether and was converted to the perchlorate from alcohol solution.

(9-Selenoxanthylo)(3-methylthia)trimethinecyanine Perchlorate (XIIc). As in the preceding experiment, this compound was obtained from 2,3-dimethylbenzothiazolium methosulfate and IIIc.

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