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PYRILOCYANINES.

36*. α-THIENYL SUBSTITUTED PYRILO- AND THIOPYRILOCYANINES

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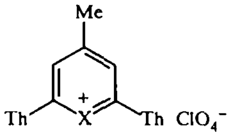
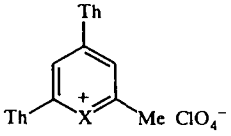
Symmetrical and nonsymmetrical 2,6- (and 4,6-)-di-α-thienyl substituted α- and γ-pyrilo- and thiopyrilocyanines have been synthesized. The effect of changing the phenyl groups for α-thienyl on the electronic absorption spectral parameters of the dyes obtained is discussed. It was found that such a change leads to a decrease in the effective length and increase in the electron donor ability of the hetero fragments containing these groups. The more intense coloring of the thienyl substituted dyes is due to interaction of the polymethine and quasilocal electronic transitions.

Polymethine dyes based on phenyl substituted pyrilium and thiopyrilium salts have been well studied (see [2] and references quoted therein). With the aim of finding polymethine dyes absorbing in the near IR region we have, in this work, synthesized analogs of the indicated dyes with thienyl residues in place of the phenyl substituents and we have studied their spectral properties. Such types of dyes have not been reported to this time.

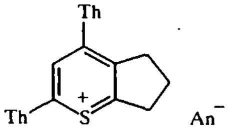
As starting materials for preparing the thienyl substituted materials we have used the pyrilium Ia [3], IIa [4] and thiopyrilium Ib, IIb, IIIa, b [4] salts.



Ia, b



IIa-b



IIIa-b

Th = α-thienyl; I, II a X = O; b X = S; III a An = ClO_4; b An = BF_4

Treatment of salt Ia with diphenylformamidine and subsequent reaction of that condensation product salt with Ia gave the trimethinecyanine IVa. Reaction of salts Ib, IIa, b, and IIIa with ethyl orthoformate gave the pyrilo- and thiopyrilocarbocyanines of the γ- and α-series (IVb, Va, b, and VI) and condensation of the thiopyrilium salts IIIa, b with corresponding electrophilic reagents (the chloride dianils of malonic, glutaconic, and 3-phenyl-2,4-dimethyleneglutaconic dialdehydes) gave the di- and tricarbocyanines (VII-IX).

Along with the above polymethine dyes of symmetrical structure, condensation of salts Ia, b to IIIa, b with para-dimethylaminobenzaldehyde gave the styryl dyes (X-XII) and reaction of the pyrilium salt Ia with 2-formylmethylene-1,3,3-trimethylindoline the unsymmetrical (pyrilo)(indo)trimethinecyanine (XIII).

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*For Communication 35 see [1].

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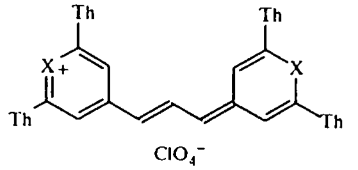
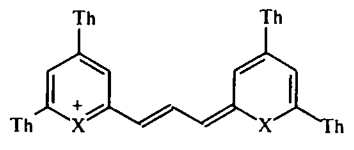
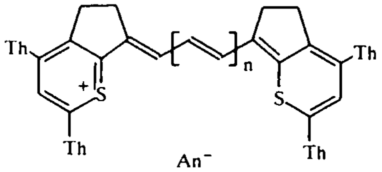


IVa, b

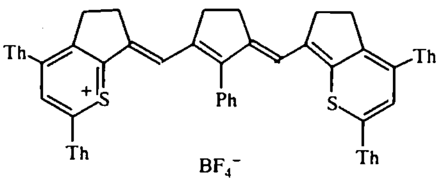


Va, b

IV, V a X = O; b X = S

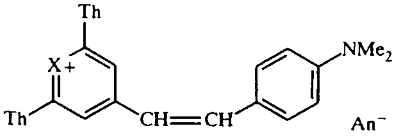


VI-VIII

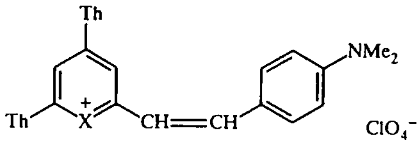


IX

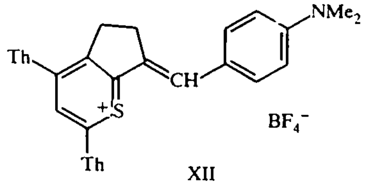
VI An = ClO_4^-, n = 0; VII An = ClO_4, n = 1;
VIII An = BF_4, n = 2



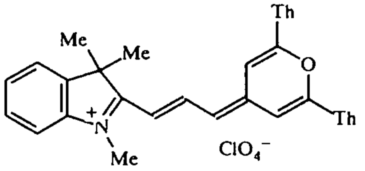
Xa, b
a An = ClO_4, X = O; b An = BF_4, X = S



XIa, b
a X = O; b X = S



XII



XIII

Table 1 compares the spectral parameters for methylene chloride solutions of the dyes synthesized by us and their known analogs containing α-thienyl groups in place of phenyl [2, 5, 6]. From the above data it is evident that the pyrilo- and thiopyrilocyanines with α-thienyl substituents absorb light at longer wavelengths that their phenyl substituted analogs. In addition, the α-pyrilo- and α-thiopyrilocyanines Va, b show a bathochromic shift larger ($\Delta\lambda$ = 70 and 95 nm) than the γ-series isomers IVa, b ($\Delta\lambda$ = 34 and 51 nm), in addition with the thiopyrilium derivatives IVb, Vb they are larger than the pyrilium analogs IVa, Va.

Within the scope of light theory [7] the effect of the heterocyclic residues on the energy of the long wavelength transition is considered in terms of lengthening of the polymethine chromophore. For quantitative evaluation of this effect there is proposed a topological index L (the so-called effective length of the end groups [8]). Moreover, the wavelength of the transition is registered as $\lambda_n = V(n + L)$, where V = 100 nm, the vinylene shift, and n is the number of vinylene groups in the chain. Hence the parameter L indicates a number of vinylene groups related to the equivalent end groups from the λ_{max} position. In fact, selection of heterocyclic residues having a large effective length is one of the basic pathways for shifting the absorption of polymethine dyes to the long wavelength region. However, calculation has shown that change of phenyl residues for α-thienyl leads to a decrease in the effective length of $\Delta L = 0.39$ for the pyrilium residue and 1.07 for thiopyrilium. Hence the bathochromic shift of the absorption band on going from the phenyl substituted pyrilo- and thiopyrilocyanines to their α-thienyl substituted analogs has another cause. It is known that, if the heterocycles have a particularly intense absorption, there may arise in the short wavelength region of the spectra of the dyes bands corresponding to the so-called quasilocalized transitions between the MO localized principally on the end residues and the delocalized polymethine MO. In the case of closely related polymethine and localized transitions they can interact such that the energy of the former of these can be decreased and the second increase [9]. From Table 1 it is apparent that, in the spectra of the α-thienyl substituted dyes, there are observed bands in the 400-500 nm region which are shifted by 70-80 nm to long wavelength of those of the phenyl substituted analogs. In the starting salts a similar change is accompanied by analogous shifts in the long wavelength band. Thus, interaction of the

TABLE 1. Spectral Parameters for α-Thienyl Substituted Salts and Dyes and Their Phenyl Substituted Analogs in Methylene Chloride

Compound	Maximum absorption, λ_{max}, nm (molar extinction coefficient, $\varepsilon \times 10^{-4}$)		
	α-thienyl substituted	phenyl substituted	$\Delta\lambda$[*]
Ia	304, 330, 470 (1,78; 1,33; 2,66)	241,281, 402 (1,28; 1,54; 2,29)[†]	
Ib	280, 340, 492 (2,62; 0,62; 2,65)	267, 326, 405 (2,89; 0,39; 2,06)	
IIa	279, 334sh, 378, 443 (1,07; 0,67; 2,05; 4,40)	260, 355, 384 (1,05; 1,62; 1,64)	
IIb	260, 305, 415, 458 (0,74; 1,14; 2,34; 2,64)	253, 278 sh, 372 (1,04; 0,81; 2,61)	
IVa	460, 660, 720 (2,3; 5,46; 27.5)	396, 633, 686 (2,7; 5,3; 25,2)	34
IVb	482, 736, 813 (2,2; 4,6; 22,6)	402, 700, 762 (2,1; 4,6; 24,6)	51
Va	781, 870	360, 395, 730, 800 (2,8; 2,7; 5,7; 8,5)	70
Vb	449, 868, 960 (3,5; 4,3; 6,6)	375, 865 (2,3; 7,2)	95
VI	470, 926, 1050 (2,7; 4,2; 8,87)	441, 865, 965 (1,51; 4,75; 10,07)	85
VII	460, 505, 1010, 1145 (1,72; 1,66; 6,02; 12,96)	486, 940, 1055 (1,39; 7,2; 16,6)	90
VIII	430, 1125, 1275 (2, 15; 6,2; 7,9)	539, 1050, 1180 (1,4; 11,1; 14,46)	95
IX	430, 1175, 1360 (1,9; 5,41; 9,33)	589, 1105, 1262 (1,1; 7,3; 11,0)	98
Xa	460, 670 (1,9; 11,5)	393, 656 (1,89; 10,8)	14
Xb	470, 726 (1, 69; 9,54)	396, 695	55
XIa	419, 716 (5,3; 5,44)	389, 427, 675, (2,0; 4,32; 4,77)	41
XIb	445, 760 (3,74; 4,55)	450, 717	43
XII	440, 790 (4,0; 6,1)	423, 446, 715 (1,02; 1,05; 5,11)	75
XIII	420, 608, 651 (0,9; 4,75; 6,53)	374, 595, 632 (1,37; 7,42; 8,92)	19

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[*] $\Delta\lambda$) is the bathochromic shift of the long wavelength absorption of changing from Ph- to α-thienyl substituted dye.

[†] Data for compounds I-II taken from [4].

local and polymethine transitions also apparently leads to deeper coloring of the thienyl substituted dyes. In fact, the short wavelength bands of all the thienyl substituted dyes are shifted hypsochromically with respect to the bands of the corresponding salts whereas such a dependence is not observed for the phenyl derivatives. The magnitude of this interaction is probably due to the larger bathochromic shift for the thiopyrilocyanines compared to the pyrilocyanines and for the dyes of the α-series compared with their γ-isomers. In terms of the discussed effect above, the deepening of the color for the thienyl substituents should be retained in the vinylogous series of dyes, and this is observed for compounds VI-VIII.

It should be mentioned that, thanks to the above effect, α-thienyl substituted pyrilo- and thiopyrilocyanines absorb significantly more intensely than other polymethine dyes. Further deepening of the color can be achieved by fixing their polymethine chains via bridging groups [10]. As a result of the simultaneous action of these two factors the carbocyanine VI (λ_{max} 1050 nm) and tricarbocyanine IX (λ_{max} 1360 nm) absorb light at the longest wavelength of all known polymethine dyes with the same chromophore length.

An important characteristic effect of the heterocyclic residues on the position of the electronic levels in the polymethine dye molecules is their relative basicity or, more strictly, electron donor ability (Φ_0) [8]. This value typifies a shifting of the boundary orbitals of the dye relative to the orbital of the unsubstituted polymethine chain. The symmetrical polymethine dyes, containing hetero residues with an average value of Φ_0 (45°), are characterized by maximal fit of the order of π-bonds and minimum change on photoexcitation thanks to which they can be more stable and have a larger absorption selectivity than dyes with hetero residues of high or low electron donor ability.

The phenyl substituted pyrilo- and thiopyrilocarbocyanines are characterized by low electron donor abilities (35.5° and 34.9° respectively) [11], i.e., their boundary levels are slightly down when compared with dyes of average electron donor ability and so an increase in the indicated property for this type of dye is present. It did not appear possible to determine this

TABLE 2. Parameters for Compounds Synthesized

Compound	Empirical formula	Found, % / Calculated, %		mp, °C	Yield, %
		Cl	S		
IVa	$C_{29}H_{19}ClO_6S_4$	$\underline{5,4}$ 5,6	$\underline{20,2}$ 20,4	> 250	48
IVb	$C_{29}H_{19}ClO_4S_6$	$\underline{5,4}$ 5,4	$\underline{29,2}$ 29,2	> 300	60
Vb	$C_{29}H_{19}ClO_4S_6$	$\underline{5,4}$ 5,4	$\underline{28,8}$ 29,2	189...190	37
VI	$C_{33}H_{23}ClO_4S_6$	$\underline{4,9}$ 5,0	$\underline{26,8}$ 27,0	> 300	82
VII	$C_{35}H_{25}ClO_4S_6$	$\underline{4,8}$ 4,8	$\underline{26,0}$ 26,1	> 300	61
VIII	$C_{37}H_{27}BF_4S_6$	—	25,6 25,6	> 300	56
IX	$C_{45}H_{33}BF_4S_6$	—	$\underline{22,6}$ 22,6	> 300	50
Xa	$C_{23}H_{20}ClNO_5S_2$	—	$\underline{13,6}$ 13,1	280...281	69
Xb	$C_{23}H_{20}NBF_4S_3$	—	$\underline{19,2}$ 19,5	217...218	87
XIa	$C_{23}H_{20}ClNO_5S_2$	$\underline{7,4}$ 7,2	$\underline{12,8}$ 13,1	277...278	43
XIb	$C_{23}H_{20}ClNO_4S_3$	$\underline{6,8}$ 7,0	$\underline{18,6}$ 19,0	239...240	50
XII	$C_{25}H_{22}NBF_4S_3$	—	$\underline{18,3}$ 18,5	210...212	40
XIII	$C_{27}H_{24}ClO_5S_2$	$\underline{6,4}$ 6,7	$\underline{12,4}$ 12,1	186...188	37

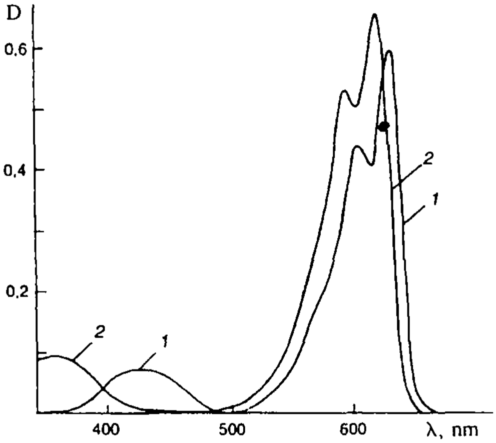

Fig. 1. Absorption spectra in methylene chloride of: 1) indopyrilocarbocyanine XIII; 2) phenyl substituted analog of XIII (C ~ $1 \cdot 10^{-5}$ g-mol/liter).

change when substituting α-thienyl residues for phenyl via calculation of the deviation (D)* for the unsymmetrical dyes X-XIII. This method is inapplicable when the starting symmetrical parent dyes are significantly different in the region of absorption [14] or the short wavelength band of one of them is displaced to the same region as the long wavelength band of the other [15]. In this case even a negative deviation can arise. This is also shown for the styryl dyes Xa, b and carbocyanine XIII, values of D being −4, −14, −15 nm, and for the phenyl substituted analogs (D −7, −8, −14 respectively). Nonetheless, the calculation shows that the electron donor ability of the discussed hetero residues when changing their phenyl groups for α-thienyl increases ($\Delta\Phi_0$ = 10°). If this is so, the electron asymmetry of the dye XIII should be lower than its phenyl substituted analog and should be accompanied by a decrease in the intensity of the transition to the vibrational sublevel. In fact, for the

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*D is the deviation of the maximum absorption of the unsymmetrical dye from the arithmetic mean of the maxima of the two "parent" dyes of symmetrical structure.

first of the dyes the ratio of the intensity of the ground and vibrational transitions amounts to $\varepsilon_1/\varepsilon_2 = 1.37$ while for the second the value of $\varepsilon_1/\varepsilon_2$ is 1.20 (Fig. 1).

EXPERIMENTAL

Electronic absorption spectra for the compounds synthesized were measured on an SF-20 spectrophotometer. The purity of the synthesized materials was monitored by TLC on Silufol UV-254 plates using acetonitrile–chloroform eluent (1:1). To calculate the effective length and the electron donor ability the same parameters were used for the atoms and bonds as in [11] as were the rotation of the phenyl and α-thienyl substituents relative to the pyrilium and thiopyrilium rings.

The parameters for the compounds synthesized are given in Tables 1 and 2.

2,6-Di(α-thienyl)-4-{3-[2,6-di(α-thienyl)pyran-4-ylidine]prop-1-en-1-yl}pyrilium Perchlorate (IVa). A mixture of Ia (0.8 mmole) and diphenylformamidine (1.1 mmole) was fused for 5 min at 150°C. After cooling, the melt was dissolved in acetonitrile and 2,6-di(α-thienyl)-4-anilinovinylpyrilium perchlorate was precipitated using a 20% solution of perchloric acid. The intermediate product was filtered and washed with water, acetic acid, and ether. Yield 54%. A mixture of this perchlorate (0.44 mmole), salt Ia (0.44 mmole), and anhydrous sodium acetate (0.44 mmole) in acetic anhydride (1.5 ml) was held at 130°C for 1 h. After cooling the reaction mixture, the precipitate was filtered and washed with acetic acid and ether and crystallized from a mixture of acetic acid and acetonitrile (1:1).

2,6-Di(α-thienyl)-4-{3-[2,6-di(α-thienyl)thiopyran-4-ylidene]prop-1-en-1-yl}thiopyrilium Perchlorate (IVb). A mixture of salt Ib (0.5 mmole), ethyl orthoformate (0.7 mmole), and anhydrous sodium acetate (0.5 mmole) in a mixture of acetic acid and acetic anhydride (1:1, 1 ml) was held at 130°C and treated as described above for dye IVa.

4,6-Di(α-thienyl)-2-{3-[4,6-di(α-thienyl)thiopyran-4-ylidene]prop-1-en-1-yl}thiopyrilium perchlorate (Vb) was prepared similarly to perchlorate IVb from salt IIb.

2,4-Di(α-thienyl)-7-{[2,4-di(α-thienyl)-5,6-dihydrocyclopenta[b]thiopyran-7-yl]methylidene-5,6-dihydrocyclopenta[b]thiopyrilium perchlorate (VI) was prepared similarly to perchlorate Vb from salt IIIa but, in place of sodium acetate, there was added pyridine (0.5 mmole) and the reaction mixture was refluxed for 3 min. The product was precipitated from acetonitrile using 20% perchloric acid to effect purification.

2,4-Di(α-thienyl)-7-{3-[2,4-di(α-thienyl)-5,6-dihydrocyclopenta[b]thiopyran-7-yl]prop-2-en-1-ylidene}cyclopenta[b]thiopyrilium perchlorate (VII) was prepared from salt IIIa and the chloride dianil of malondialdehyde similarly to salt IVb with the reaction mixture being held for 5 min at 130°C.

2,4-Di(α-thienyl)-7-{5-[2,4-di(α-thienyl)cyclopenta[b]thiopyran-7-yl]penta-2,4-dien-1-ylidene}cyclopenta[b]thiopyrilium tetrafluoroborate (VIII) was prepared similarly to perchlorate VII from salt IIIb and the chloride dianil of glutaconic dialdehyde.

The tricarbocyanine (IX) was synthesized by the method of synthesis of perchlorate VII from salt IIIb and phenyl[5-phenylamino-2,4-dimethylene-3-phenyl]penta-2,4-dienylideneammonium chloride.

2,6-Di(α-thienyl)-4-[β-4-(dimethylaminophenyl)ethenyl]pyrilium perchlorate (Xa), 2,6-di(α-thienyl)-4-[β-4-dimethylaminophenyl)ethenyl]thiopyrilium tetrafluoroborate (Xb), 4,6-di(α-thienyl)-2-[β-4-(dimethylaminophenyl)ethenyl]pyrilium perchlorate (XIa), and the thiopyrilium perchlorate analog (XIb), and 2,4-di(α-thienyl)-7-(4-dimethylaminophenylmethylene)-5,6-dihydrocyclopenta[b]thiopyrilium tetrafluoroborate (XII) were obtained by holding an equimolar amount of the corresponding salts Ia, b, IIa, b, or IIIb with para-dimethylaminobenzaldehyde for 5 min at 140°C. The products were crystallized from acetic anhydride or acetonitrile.

1,3,3-Trimethyl-2-{3-[2,6-di(α-thienyl)pyran-4-ylidene]prop-1-en-1-yl}indolium perchlorate (XIII) was prepared from salt Ia (1 mmole), 1,3,3-trimethyl-2-formylmethyleneindoline (1 mmole), and anhydrous sodium acetate (1 mmole) by holding the reaction mixture at 130°C for 15 min. The product was purified similarly to compound VI.

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