PYRYLOCYANINES.

13.* SYMMETRICAL PYRYLOCYANINES BASED ON 2,3-POLYMETHYLENE-4,6-DIPHENYLPYRYLIUM SALTS

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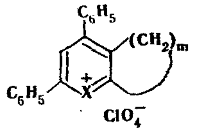
Symmetrical 4,6,4',6'-tetraphenyl-substituted pyrylo-2-, thiopyrylo-2-, and pyrylo-2-cyanines in which both α positions of the polymethine chain are bonded to the β positions of the heterocyclic residues by ethylene and trimethylene groups were synthesized. The introduction of bridged groupings is accompanied by intensification of the fine structure and bathochromic and hypsochromic effects in the absorption spectra; the former effect is greater and the latter effect is smaller in the case of ethylene groups. The steric and electronic effects of these groups are discussed with the aid of PMR spectroscopy and quantum chemistry.

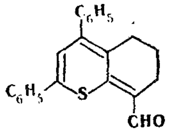
In series of polymethine dyes constructed from nitrogen heterocycles, cyanines with polymethylene groupings that connect individual links of the polymethine chain both between themselves [2] and with the heteroresidues [3] have been studied in rather great detail. These groupings affect the color [4], basicity [5], and other properties of dyes that are of practical importance. A great deal less is known about pyrylocyanines with polymethylene groupings, although such dyes are more stable than their analogs with an unsubstituted chromophore [6, 7], and some pyrylo-2-cyanines of this type can be used as inert shutters for lasers [8].

Within the framework of our systematic study of pyrylocyanines it seemed of interest to study the effect of polymethylene groupings on their color. In the present paper we describe the results of an investigation of symmetrical pyrylo-2-cyanines and their sulfur- and nitrogen-containing analogs in which the α,α' positions of the polymethine chromophore are connected with the β-carbon atoms of the heterocyclic residues by ethylene or trimethylene groupings (Table 1).

For the synthesis of the examined dyes we used salts with I and II structures and 2,4-diphenyl-6,7-dihydro-5H-1-benzothiopyran-8-al (III), which we obtained by saponification of the product of condensation of thiopyrylium salt IIb with dimethylformamide (DMF). Trimethylidynecyanines with five-membered groupings (IVa-b) were obtained by condensation of salts Ia,b with ethyl orthoformate [9]. Pyrylotrimethylidynecyanine VIIa containing six-membered groupings was similarly synthesized. Let us note that an attempt by Kirner and Wizinger [10] to synthesize this dye by condensation of pyrylium salt IIa with 2,4-diphenyl-8-(ethoxymethylidene)-5,6,7,8-tetrahydrobenzo[b]pyrylium perchlorate was unsuccessful. We were able to obtain thiopyrylomethylidynecyanine VIIb by condensation of thiopyrylium salt IIb with ω-aldehyde III. Pentamethylidynecyanines Va-b and VIIIb and heptamethylidynecyanine VIa were



Ia-c, IIa,b



III

I m=2; II m=3; a X=O; b X=S; c X=Se

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*See [1] for Communication 12.

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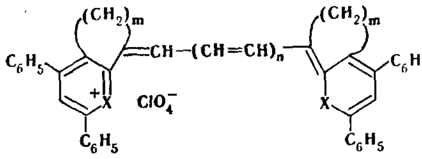
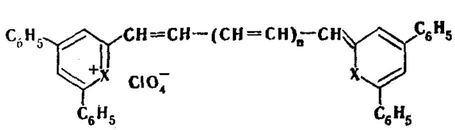
TABLE 1. Characteristics of the Long-Wave Absorption Bands of Solutions of Dyes IV-XI in CH_2Cl_2

Compound	X	m	n	λ_{max}, nm(lg ε)	M^{-1}, nm	f	σ, cm^{-1}	γ_1	γ_2	F
IVa	O	2	0	775; 865 (4,82; 5,08)	800,6	0,72	1085	1,32	2,6	0,103
Va	O	2	1	855; 960 (4,76; 5,11)	894,9	1,06	1061	1,78	5,2	0,131
VIa	O	2	2	956; 1080 (5,04; 5,37)	1012,6	1,43	1068	0,71	3,5	0,095
VIIa	O	3	0	760; 835 (4,59; 4,79)	781,9	0,51	1146	1,26	2,7	0,074
VIIIa	O	3	1	845; 940 (4,88; 5,14)	874,4	0,96	1071	1,44	3,4	0,092
IXa	O	3	2	934; 1050 (4,92; 5,20)	971,9	1,07	1022	1,47	3,4	0,099
Xa	O	—	0	730; 800 (4,77; 4,93)	739,6	0,78	1176	1,17	2,2	0,064
XIa	O	—	1	820; 910 (4,91; 5,08)	839,5	1,12	1137	1,32	2,9	0,083
IVb	S	2	0	865; 965 (4,68; 5,00)	907,0	0,67	894	1,13	1,6	0,068
Vb	S	2	1	940; 1055 (4,86; 5,22)	991,0	0,95	904	1,45	3,2	0,095
VIIb	S	3	0	860 (4,73)	830,1	0,59	1135	0,83	2,0	0,033
VIIIb	S	3	1	1025 (4,94)	956,0	0,78	1061	1,29	2,9	0,060
Xb	S	—	0	865 (4,85)	820,2	0,79	1058	1,07	1,8	0,046
XIb	S	—	1	905; 1000 (4,85; 5,03)	926,1	0,97	1072	1,25	2,7	0,062
IVc	NCH_3	2	0	735 (4,79)	691,7	0,67	1300	1,48	3,7	0,078
Vc	NCH_3	2	1	815 (5,14)	779,4	0,72	1010	1,65	4,5	0,087
VIIc	NCH_3	3	0	714 (4,40)	671,1	0,30	1430	1,46	3,7	0,080
VIIIc	NCH_3	3	1	810 (4,77)	766,8	0,53	1180	1,58	4,2	0,084
Xc	NCH_3	—	0	630 (4,97)	604,6	0,88	1060	1,00	2,0	0,041
XIc	NCH_3	—	1	728 (—)	701,8	—	1023	1,50	4,3	0,073

obtained in the same way as dyes VIIIa and IXa [11] by condensation of the corresponding pyrylium salts with malonic or glutaconic aldehyde anilanilide hydrochloride. Pyridocyanines IVc, Vc, VIIc, and VIIIc were obtained by treatment of the corresponding pyrylocyanines with methylamine.


IV–Va -c VI a; VII–VIIIa -c, IX a


X–XIa -c

a X=O; b X=S; c X=NCH_3

The spectral characteristics of the synthesized α-pyrylocyanines and their heteroanalogs are compared with the corresponding characteristics of unsubstituted dyes Xa-c and XIa-c in Table 1. In addition to the generally accepted characteristics of the long-wave absorption bands (λ_{max}, log ε, and f), as in [1], the average positions of the absorption bands (M^{-1}), the characteristics of the form of the bands and the widths (σ), and the coefficients of the asymmetry (γ_1), excess (γ_2), and fine structure (F) are also presented. It follows from the data presented in Table 1 that the introduction of polymethylene bridged groups leads to deepening of the color; the effect of ethylene groups is greater than that of trimethylene groups. With only one exception (dye VIIb), this conclusion follows from a comparison of the maxima and is strictly observed for the average positions of the absorption bands. The greatest effects are observed in series of pyridine derivations, and trimethylene groups have a significant effect in this case.

The explanation for the effect of the bridged groups should be sought in their electronic and steric effects. In contrast to unsubstituted dyes, dyes with polymethylene "bridges" have a fixed di-cis conformation of the polymethine chain (Fig. 1). In the case of pyridine derivatives (X = NCH_3) this conformation may not be planar because of the steric hindrance between the methyl groups and the hydrogen atoms of the polymethine chain. The particularly great bathochromic effects in the case of pyridocyanines [12] should be ascribed precisely to disruption of the coplanarity of the chromophore molecule. The unsubstituted dyes of this series may exist in a planar everywhere-trans conformation, but the conformational difference per se should not have a substantial effect on the position of the absorption band [13]. The marked decrease in oscillator force f (by a factor of more than 2) and the extinction at the maximum (by a factor of almost four) vis-à-vis a significant broadening of the absorption band indicates substantial disruption of the coplanarity in the dye molecule with trimethylene groups (VIIc). These effects are expressed to a smaller extent in the case of its analog with ethylene groups (IVc); this is evidently associated with an increase in the angle

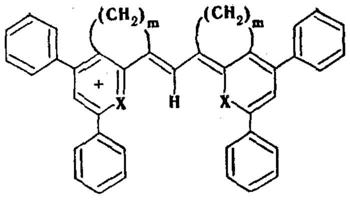


Fig. 1. Conformation of dyes IV-XI.

TABLE 2. Theoretical Absorption Maxima of Dyes XII

R_1	R_2	λ_{max}, nm, for X		
		O	S	NCH_3
H	H	475	555	480
$—CH_2—CH_2—$		685	822	689
$—CH_2—CH_2—CH_2—$		606	725	616

between the polymethine chain and the $N—CH_3$ bond. In addition, steric hindrance directly between the methylene groups of the bridges, which is also increased for the trimethylene groups (m = 3), is not excluded in the case of carbocyanines (n = 0). It is manifested as a considerable contraction of the absorption bands on passing from dyes IVc and VIIc to the corresponding pyridodicarbocyanines Vc and VIIIc, for which steric hindrance of this sort is not possible. Let us note that a slight decrease in the oscillator forces is also observed in the case of all pyrylo- and thiopyrylocyanines with polymethylene bridges as compared with the unsubstituted dyes, despite the fact that the extinctions at the maxima and the coefficients of the asymmetry, excess, and fine structure usually increase (always in the case of ethylene bridges), whereas the widths of the absorption bands decrease (with the single exception of dye VIIb) (see Table 1). Such changes in the parameters of the absorption bands might have been expected only in the case of slight disruptions of the coplanarity of the polymethine chromophore. The somewhat greater decrease in the oscillator forces in the case of thiapyrylocyanines and carbocyanines (n = 0) as compared with dicarbocyanines (n = 1) could indicate that such disruptions do make their contribution, since intensification of steric hindrance precisely in the vicinity of the polymethine chain might be expected in these cases. However, such effects are not expressed. On the other hand, a decrease in the oscillator forces on passing from ethylene bridges to trimethylene bridges is clearly expressed in all cases without exception. An examination of Dreiding models shows that the bridged groupings may affect not only the coplanarity of the chromophore but also the conformation of the phenyl groups in the γ positions of the heteroresidues by disrupting their conjugation with the overall chromophore system. A direct confirmation of the greater magnitude of the torsion angle between the indicated phenyl substituents and the planes of the heterorings in compounds with a six-membered grouping follows from an analysis of the PMR spectra of pyrylium salts Ia and IIa and their thio analogs Ib and IIb. The chemical shift (δ) of the proton in the β position of pyrylium salt IIa, which contains a six-membered ring, is shifted 0.14 ppm to strong field as compared with the signal of the analogous proton of pyrylium salt Ia, which contains a five-membered ring.

Precisely the same difference is also observed between the positions of the β-H signals of thiopyrylium salts IIb and Ib. The relationship between the contribution to the change in δ due to the phenyl ring currents and to the shielding of the o-H atoms in biphenyl derivatives and the magnitude of the torsion angle between the individual aromatic rings [14] makes it possible to estimate the difference in the angles of rotation of the phenyl substituents in the examined compounds. The indicated torsion angle in salts IIa,b, which contain a six-membered ring, is ~16° greater than in salts Ia,b, which contain a five-membered ring. Let us note that considerably greater but also closer shifts (−0.46 and −0.49 ppm) are observed for the signals of the protons of the CH_2 groups adjacent to the β position of the heterorings on passing from pyrylium and thiopyrylium salts Ia,b to their higher homologs IIa,b. However, the latter is due not only to the difference in the shielding of the CH_2 groups by the adjacent phenyl groups but also to the specific characteristics of the rings themselves. An estimate made jointly with M. Yu. Kornilov on the basis of simple geometrical constructions led to torsion angles of 52.4 and 68° for compounds with five-membered and six-

TABLE 3. Characteristics of the Synthesized Compounds

Compound	mp,* °C	Found,† %			Empirical formula	Calculated, %			Yield, %
		Cl	N	S		Cl	N	S	
III	133—144			9,7	$C_{22}H_{19}OS$			9,7	40
Va	240	4,9			$C_{43}H_{33}ClO_6$	5,2			64
VIa	227—228	5,2			$C_{45}H_{35}ClO_6$	5,2			26
VIIa	227	5,0			$C_{43}H_{35}ClO_6$	5,2			40
VIIIa	226	5,0			$C_{45}H_{37}ClO_6$	5,0			70
Vb	237	5,0		9,11	$C_{43}H_{33}ClO_4S_2$	4,9		8,9	40
VIIb	202—205	4,9		8,9	$C_{43}H_{35}ClO_4S_2$	4,9		8,9	50
VIIIb	173—175	4,8		8,3	$C_{45}H_{37}ClO_4S_2$	4,8		8,6	24
IVc	190	5,4	4,1		$C_{43}H_{37}ClN_2O_4$	5,2	4,1		35
Vc	180	5,0	3,9		$C_{45}H_{39}ClN_2O_4$	5,0	3,9		55
VIIc	170	5,2	3,9		$C_{45}H_{41}ClN_2O_4$	5,0	3,9		56
VIIIc	164	4,8	4,2		$C_{47}H_{43}ClN_2O_4$	4,8	3,8		75
XIV	241	4,1			$C_{43}H_{33}ClO_4Se_2$	4,1			29

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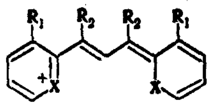
*The crystallization solvents were aqueous alcohol for III, acetic anhydride for Va, VIIIa, and XIV, acetic acid for VIIb, and ethanol for IVc and Vc.

†The compositions of dyes VIIa, VIIIa, and VIIb were also confirmed by determination of the percentages of C and H (and Se in the case of XIV).

membered rings, respectively. It is apparent that the difference between the calculated angles (∿16°) coincided with the estimate of their values of the chemical shifts of the protons. On the basis of the data presented above it may be concluded that the energy of conjugation of the phenyl groups in the γ position of the heterocyclic residues of the examined dyes with a common chromophore system in the presence of trimethylene groupings is lower ($\cos^2 68°/\cos^2 52.4° \approx 0.35$) [15] than in dyes with ethylene groupings. The deviation from the plane of the phenyl groups in the γ position is evidently the chief reason for the decrease in oscillator forces in the case of dyes with polymethylene bridges. This effect is possibly partially responsible for the higher color of dyes with trimethylene groupings as compared with ethylene groupings.

However, the fact that dyes with both ethylene and trimethylene groupings are more deeply colored than unsubstituted dyes cannot be explained only by steric factors. In this connection, let us recall that we observed distinct electronic effects in the case of symmetrical cyclization by saturated groups of the polymethine chromophore [16]. Whereas in the latter case we were able to form a judgment regarding the direction of the shift of the absorption band on the basis of only symmetry concepts, quantitative estimates are necessary in our case. In order to obtain them we calculated the absorption maxima of model dyes with the XII structure by the Hückel method [17]. The effect of saturated rings was modeled by means of the heteroatoms ($\alpha_{CH_2} = \alpha + 2\beta$). For the resonance integrals we selected the $\beta_{CCH_2} = 0.7\beta$ parameters, which are known to be too high. For the five-membered rings we assumed that $\beta_{CH_2CH_2} = 0.7\beta$, whereas we assumed that $\beta_{CH_2CH_2} = 0$ for the six-membered rings. The results of the calculation are presented in Table 2. It is apparent that allowance for the electronic effects makes it possible to expect that the introduction of polymethylene bridges should in all cases be accompanied by a bathochromic shift; the effect of an ethylene bridge should be substantially greater. The bathochromic effect could have been foreseen from the Forster—Dewar—Knott rule [12] as being a consequence of the introduction of positive substituents in even positions. Its increase in the case of ethylene bridges is not so obvious. Thus a significant part of the effect of the bridges on the position of the absorption bands of the dyes can be ascribed to direct interaction of the electrons of the saturated groups with the unsaturated chromophore and between one another.

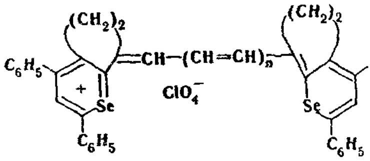


XII

As regards the forms of the absorption bands of the examined dyes, one's attention is drawn to their generally more resolved fine structure than in the case of unsubstituted dyes.

This effect is expressed quantitatively in an increase in the coefficient (F) of the fine structure (Table 1), which is particularly high in the case of pyrylocyanines with ethylene bridges. It may be associated with an increase in the rigidity of the molecules. Dye VIIb constitutes an exception in this and other respects, as we have already mentioned. Because of its unexpectedly high color the vinylene shift to dye VIIIb, which is 165 nm with respect to the maxima and reaches 125.9 nm even with respect to the average positions, is much too high. Although the spectral characteristics of this dye deviate from many comparison series, the data from the PMR spectrum leave no doubt as to its structure.

In addition to the dyes presented in Table 1 and selenopyrylocarbocyanine XIII [9], in the present research we synthesized its vinylog XIV by a method similar to that used to prepare Va,b. Dyes XIII and XIV absorb in the longest-wave region as compared with the known dyes with a polymethine chain of the same length. This is in agreement with the calculated data: The theoretical absorption maximum of dye XII is 870 nm when X = Se and $R_1 + R_2 = -CH_2CH_2-$.



XIII $n=0$. λ_{max} (log ε) 995 (5,03), XIV $n=1$. λ_{max} (log ε) 960; 1084 (4,83; 5,25)

EXPERIMENTAL

The moments of the absorption bands were determined as in [1] on the basis of the absorption spectra of the dyes at 200 cm^{-1} intervals with an SF-4A spectrometer (or an SF-8 spectrometer in the case of IVb-XIb, XIII, and XIV) in methylene chloride stabilized with 1% ethanol at layer thicknesses of 1 and 5 cm. The absorption spectra of solutions of dyes IVa,b-XIa,b were measured at 1.8-2 orders of magnitude with respect to intensity, as compared with 1.5 orders of magnitude in the case of IVc-XIc. The numerical values in Table 1 are presented with an accuracy corresponding to the degree of error in the measurement of the absorption spectra of the dyes. The PMR spectra were determined with a Tesla BS-487-B spectrometer (80 MHz) at 20°C; the solvent was CF_3COOH and the internal standard was tetramethylsilane for salts Ia,b and IIa,b, while the solvent was $CDCl_3$ and the external standard was hexamethyldisiloxane for aldehyde III and dyes VIIa,b. The quantum-chemical calculations of the dyes were carried out with a BÉSM-6 computer by means of the ÉLA program [17] with the set of parameters for the atoms and bonds taken from [18].

The purity of the preparations was monitored by thin-layer chromatography (TLC) on Silufol UV-254 plates (elution with acetonitrile).

The chemical shifts of the protons of the CH_2 groups adjacent to the β and α positions of the heteroring (β-CH_2 and α-CH_2) and of the protons in the β position (β-H) from the PMR spectra of salts Ia,b-IIa,b were as follows. For Ia: 3.39 (2H, t, β-CH_2), 3.51 (2H, t, α-CH_2), and 8.28 ppm (1H, s, β-H). For Ib: 3.38 (2H, t, β-CH_2), 3.65 (2H, t, α-CH_2), and 8.53 ppm (1H, s, β-H). For IIa: 2.93 (2H, t, β-CH_2), 3.35 (2H, t, α-CH_2), and 8.14 ppm (1H, s, β-H). For IIb: 2.89 (2H, t, β-CH_2), 3.41 (2H, t, α-CH_2), and 8.39 ppm (1H, s, β-2H).

2,4-Diphenyl-6,7-dihydro-5H-1-benzothiopyran-8-al (III). A mixture of 0.28 g (0.7 mmole) of 2,4-diphenyl-5,6,7,8-tetrahydro-1-benzothiopyrylium perchlorate (IIb)[19] and 0.51 g (7 mmole) of dimethylformamide (DMF) in 5 ml of acetic anhydride was refluxed for 15 min, after which it was cooled and treated with ether. The resulting precipitate was removed by filtration and washed with ether to give 0.29 g (89%) of 2,4-diphenyl-5,6,7,8-tetrahydro-8-dimethylaminovinyl-1-benzothiopyrylium perchlorate. A 0.29-g (0.6 mmole) sample of the latter was stirred in 10 ml of acetonitrile with 10 ml of a 5% aqueous solution (12 mmole) of sodium hydroxide at room temperature for 1 h, after which 200 ml of water was added, and the mixture was allowed to stand for 12 h. Purification of the product gave red-orange crystals with λ_{max} 470 nm (CH_3CN). PMR spectrum: 2.0 (2H, m, 6-CH_2), 2.92 (4H, m, 5-CH_2, 7-CH_2), 7.77 (11H, m, β-H, aromatic protons), and 10.2 ppm (1H, s, CHO) (Table 3).

2,4-Diphenyl-7-{3-[2,4-diphenylcyclopent-7-eno[2,3:b]pyran-7-yl]-prop-2-en-1-ylidene}cyclopenta[1,2:b]pyrylium Perchlorate (Va). A mixture of 0.5 mmole of 2,4-diphenylcyclopenta [1,2:b]pyrylium perchlorate (Ia) [20], 0.25 mmole of phenyl(3-phenylaminoprop-2-en-1-ylidene)ammonium chloride, and 0.5 mmole of anhydrous sodium acetate in 2.5 ml of a mixture

(1:1) of glacial acetic acid and acetic anhydride was heated at 110°C for 30 min, after which the dye was removed by filtration and washed with acetic acid and ether.

2,4,-Diphenyl-7-{3-[2,4-diphenylcyclopent-7-eno[2,3:b]thiopyran-7-yl]-prop-2-en-1-ylidene}cyclopenta[1,2:b]thiopyrylium Perchlorate (Vb). This compound was obtained from salt Ib [9] by the method used to prepare Va.

2,4-Diphenyl-7-{5-[2,4-diphenylcyclopent-7-eno[2,3:b]pyran-7-yl]-penta-1,3-dien-1-ylidene}cyclopenta[1,2:b]pyrylium Perchlorate (VIa). This compound was similarly obtained from salt Ia and phenyl(5-phenylaminopenta-2,4-dien-1-ylidene)ammonium chloride by heating at 137-140°C for 10 min.

2,4-Diphenyl-8-{[2,4-diphenyl-6,7-dihydro-5H-1-benzopyran-8-yl]-methylidene}-5,6,7,8-tetrahydro-1-benzopyrylium Perchlorate (VIIa). This compound was similarly obtained from 2,4-diphenyl-5,6,7,8-tetrahydro-1-benzopyrylium perchlorate (IIa) [10] and ethyl orthoformate by heating at 120°C for 1 h.

Thiopyrylocyanine VIIb. This compound was obtained from 0.2 mmole of salt IIb [19] and aldehyde III in 1.5 ml of a mixture (1:1) of acetic acid and acetic anhydride with the addition of three drops of pyridine by heating to the boiling point for 3 min. PMR spectrum: 2.2 (4H, m, 6,6-CH_2), 2.74 (1H, s, chromophore CH), 3.14 (4H, t, 7,7'-CH_2), 3.39 (4H, t, 5,5-CH_2), and 7.97 ppm (22H, m, aromatic protons and β,β'-H).

2,4-Diphenyl-8-{3-[2,4-diphenyl-6,7-dihydro-5H-1-benzopyran-8-yl]-prop-2-en-1-ylidene}-5,6,7,8-tetrahydrobenzopyrylium Perchlorate (VIIIa) and Thiopyrylocyanine VIIIb. These compounds were obtained from salts IIa,b by the method used for Va.

1-Methyl-2,4-diphenyl-7-{[1-methyl-2,4-diphenylcyclopent-1-eno[2,3:b]-pyridin-7-yl]methylidene}cyclopenta[1,2:b]pyridinium Perchlorate (IVc). A mixture of 0.5 mmole of pyrylocyanine IVa and 2 ml of a 7.5% alcohol solution of methylamine (5 mmole) in 4 ml of dimethyl sulfoxide (DMSO) was heated at 90°C for 30 min. The course of the reaction was monitored by spectrophotometry. The dye was precipitated with an aqueous solution of sodium perchlorate and purified by chromatography on aluminum oxide (elution with acetonitrile).

1-Methyl-2,4-diphenyl-7-{3-[1-methyl-2,4-diphenylcyclopent-1-eno[2,3:b]-prop-2-en-1-ylidene}cyclopenta[1,2:b]pyridinium Perchlorate (Vc). This compound was obtained from Va by the method used to prepare IVc.

1-Methyl-2,4-diphenyl-8-{[1-methyl-2,4-diphenyl-6,7-dihydro-5H-quinolin-8-yl]methylidene}-5,6,7,8-tetrahydroquinolinium Perchlorate (VIIc). This compound was obtained from IVc and VIIa by heating at 110°C for 1.5 h. The dye was washed with alcohol.

1-Methyl-2,4-diphenyl-8-{3-[1-methyl-2,4-diphenyl-6,7-dihydro-5H-quinolin-8-yl]prop-2-en-1-ylidene}-5,6,7,8-tetrahydroquinolinium Perchlorate (VIIIc). This compound was obtained from VIIIa by the method used to prepare VIIc.

Selenopyrylocyanine XIV was obtained from salt Ic by the method used to obtain Va.

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THIAZOLE ANALOGS OF CHALCONE AND FLAVONE

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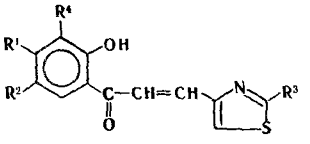
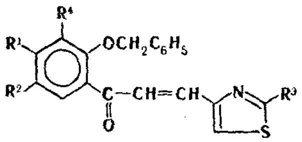
New thiazole analogs of chalcones and their epoxides were obtained. Thiazole analogs of flavone and isoflavone were synthesized for the first time on the basis of these compounds. It is shown that o-hydroxyphenylpyrazole derivatives are formed by the action of hydrazine hydrate on 2-(4-thiazolyl)chromones. The PMR spectra of the new substances are presented and discussed.

Continuing our research [1] on 2-hetarylchromones we have realized the synthesis of chromones that contain a thiazole ring in the 2 position of the pyrone ring. We became interested in these compounds because of the prevalence of the thiazole ring among natural biologically active substances and also because of the fact that some thiazole analogs of isoflavones display considerable hypolipidemic activity [2]. Thiazole analogs of chalcone (Ia-j), which were obtained by condensation of the corresponding o-hydroxyacetophenones with 2-methyl- or 2-phenyl-4-formylthiazole [3] by the method in [4], served as the starting compounds for the synthesis of 2-thiazolylchromones.



Ia-j



IIa-f

o-Benzyloxyacetophenones, which were in turn obtained by alkylation of o-hydroxyacetophenones with benzyl bromide, were used for the synthesis of thiazolylpropenones IIa-f with a protected hydroxy group in a similar condensation.

Thiazole analogs (I and II) of chalcones are primarily high-melting, crystalline, yellow compounds that are quite soluble in organic solvents. To confirm their structure we used NMR spectroscopy. The physical constants and spectral characteristics of the synthesized compounds are presented in Table 1. A narrow singlet of a hydroxy proton is observed in the PMR spectra of thiazolylpropenones Ia-j at weakest field (12.38-13.42 ppm). Its position in the spectrum changes somewhat from compound to compound; however, no correlation between the chemical shift of the signal of the hydroxy proton and the electronegativities or volumes of

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