II according to the PMR data. Acids IIb-f were similarly obtained. The physicochemical constants of the compounds obtained are presented in Table 2.

3-(p-Acetamidophenyl)-6-hydroxyphthalic Acid (IIIa). A 0.5-g sample of anhydride Ia was dissolved by heating in 5 ml of 10% NaOH, after which the solution was cooled and acidified with 2 N HCl. The resulting crystals were removed by filtration, washed with water, and dissolved in ether. The ether solution was dried over $CaCl_2$ and evaporated, and the precipitated IIIa was removed by filtration and washed with petroleum ether. Acids IIIb,c were similarly obtained. The physicochemical constants of the compounds obtained are presented in Table 3.

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PYRYLOCYANINES.

15.* BENZOPYRYLO-2-CYANINES

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Symmetrical 4,4'-diphenyl-substituted benzopyrylo-2-monomethylidyne, carbo-, and dicarbocyanines and their thio analogs, as well as unsymmetrical carbocyanines that contain, in addition to 4-phenylbenzopyrylium or 4-phenylbenzothiopyrylium rings, 3-ethylbenzothiazolium or 1,3,3-trimethyl-3H-indolium residues, were synthesized. The indicated dyes were more highly colored than their isomers that contain flavylium or thioflavylium residues. On the basis of the deviations calculated from the centers of the absorption bands it was concluded that the benzopyran residues in the dyes of the α series have greater electron donor character than those in the dyes of the γ series.

In the present research we set out to synthesize and investigate the color of benzopyrylo-2-cyanines, which, in contrast to the corresponding 4-substituted isomers [2], have not been investigated systematically. The synthesis of such dyes is fraught with certain difficulties because of the ease of self-condensation of 2-methylbenzopyrylium salts in the 4 position. This was evidently precisely the reason for the color ascribed to the 2-methylbenzopyrylium salt (λ_{max} 590 nm [3]). Considering the information stated above, we dealt with 4,4'-diphenyl-substituted dyes, of which only benzopyrylo-2-monomethylidynecyanine was previously known [4]. In the synthesis of the indicated dyes we used 2-methyl-4-phenylbenzopyrylium salts (I) [5] and benzothiopyrylium salts (II), as well as their analogs without substituents in the 2 position, viz., III and IV [6], respectively, and, in addition, 2-formylmethylene-4-benzopyran (V) and benzothiopyran (VI).

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*See [1] for communication 14.

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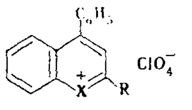
TABLE 1. Characteristics of the Long-Wave Absorption Bands of Solutions of Symmetrical Benzopyrylocyanines in CH_2Cl_2

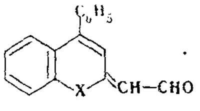
Compound	X	n	λ_{max}, nm	lg ε	M^{-1}, nm	f	σ, cm^{-1}	γ_1	γ_2	F
VIIa	O	0	500, 532, 575	4,27; 4,74; 4,97	545,5	0,74	1204	1,31	2,6	0,085
b			602	4,88	586,8	0,60	944	1,03	2,2	0,037
VIIIa	O	1	655, 713	4,77; 5,03	670,0	0,86	1084	1,25	2,5	0,071
b			715	5,31	695,9	0,83	772	1,60	3,4	0,110
IXa	O	2	740, 815	4,99; 5,36	774,9	1,44	957	1,32	2,4	0,088
b			825	5,45	795,8	1,25	797	1,61	3,4	0,120
Xa	S	0	598	5,04	583,2	0,75	938	1,02	2,3	0,044
b			700	4,87	686,9	0,53	815	1,02	2,2	0,034
XIa	S	1	780	5,08	759,1	0,94	901	1,08	1,7	0,045
b			800	—	779,6	(0,55)	726	1,70	4,9	0,096
XIIa	S	2	905	5,26	862,7	1,26	888	1,28	2,4	0,066
b			914	5,31	878,5	1,01	801	1,61	4,0	0,098

TABLE 2. Characteristics of the Long-Wave Absorption Bands of Solutions of Unsymmetrical Dyes in CH_2Cl_2

Compound	X	Y	R	λ_{max}, nm	lg ε	M^{-1}, nm	D_M, nm	f	σ, cm^{-1}	γ_1	γ_2	F
XIIIa	O	$C(CH_3)_2$	CH_3	605, 650	4,86; 4,69	586,4	11,6	1,07	1514	0,82	1,1	0,030
b				595, 640	4,69; 4,66	586,8	24,2	0,72	1593	1,09	2,8	0,053
XIVa	S	$C(CH_3)_2$	CH_3	644, 694	4,77; 4,62	626,4	16,2	0,85	1435	0,80	1,1	0,029
b				633, 676	4,85; 4,82	624,5	28,3	0,98	1414	1,12	2,5	0,043
XVa	O	S	C_2H_5	590, 631	4,82; 4,64	571,8	35,8	1,06	1599	0,84	1,2	0,030
b				585, 627	4,81; 4,76	573,9	46,6	0,96	1504	1,00	1,6	0,042
XVIa	S	S	C_2H_5	620 (676),	4,77; (4,56)	605,9	46,2	0,94	1547	0,82	1,2	0,028
b				617	—	603,2	59,2	—	1621	1,18	2,8	0,050



I–IV

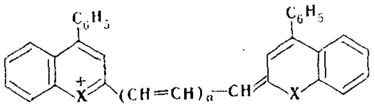


V–VI

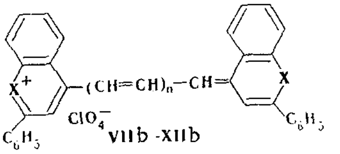
I, III, V X = O; II, IV, VI X = S; I, II R = CH_3; III, IV R = H

Salts I-IV were synthesized by the reaction of the corresponding chromones or their thio analogs with phenylmagnesium bromide. Aldehydes V and VI were obtained by saponification of the products of aminoformylation of salts I and II by the method in [7].

Monomethylidynecyanines VIIa and Xa [4] (Table 1) were synthesized by condensation of 2-methyl-substituted salts I and II with the corresponding 2-unsubstituted salts III and IV, while symmetrical carbocyanines VIIIa and XIa were synthesized by the reaction of salts I and II with ethyl orthoformate and also by condensation of the same salts with aldehydes V and VI. Dicarbocyanines IXa and XIIa were synthesized from salts I and II and (3-phenylaminopropen-2-ylidene)phenylammonium chloride.



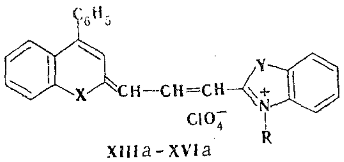
VIIa–XIIa



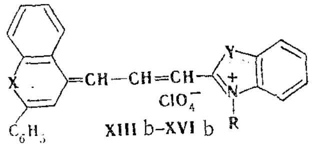
VIIb–XIIb

In addition to polymethine dyes with a symmetrical structure, by condensation of salts I and II with 2-formylmethylene-1,3,3-trimethylindoline we obtained unsymmetrical (benzo-2-pyrylo)(indo)trimethylidynecyanines XIIa and XIVa, and unsymmetrical (benzo-2-pyrylo)(thia)-

trimethylidynecyanines XVa and XVIa were obtained from aldehydes V and VI and 2-methyl-3-ethylbenzothiazolium iodide.



XIIIa-XVIa



XIII b-XVI b

XIII $X=O$, $Y=C(CH_3)_2$, $R=CH_3$; XIV $X=S$, $Y=C(CH_3)_2$, $R=CH_3$; XV $X=O$, $Y=S$, $R=C_2H_5$; XVI $X=S$, $Y=S$, $R=C_2H_5$

The spectral characteristics of the synthesized 4,4'-diphenylbenzo-2-pyrylocyanines are compared with the analogous characteristics of the isomeric flavylo- and thioflavylocyanines VIIb-XVIb [2], which were determined in the present research under conditions comparable to those for the investigated dyes, in Tables 1 and 2. In addition to the generally accepted characteristics of the long-wave absorption bands (λ_{max}, log ε, and oscillator forces f), as in [1], the average positions of the absorption bands (M^{-1}) and the characteristics of the form of the bands, viz., the widths (σ) and the coefficients of asymmetry (γ_1), excess (γ_2), and the fine structure (F), are presented. For the dyes with an unsymmetrical structure (Table 2) the deviations (D_M) determined from the M^{-1} values of the unsymmetrical and corresponding symmetrical dyes are also presented.

Let us initially examine the principles in the absorption spectra of carbo- and dicarbocyanines in order to exclude the effects associated with the close location of the heterocyclic residues in monomethylidynecyanines. It is apparent from the data presented in the tables that symmetrical benzo-2-pyrylocyanines VIIIa and IXa and their sulfur analogs XIa and XIIa are somewhat more highly colored than the corresponding γ isomers VIIIb, IXb, XIb, and XIIb. The opposite effect is observed for tetraphenyl-substituted pyrylo- and thiopyrylocyanines — the dyes of the α series are more deeply colored than those of the γ series (by 100-110 nm) [7]. This difference can be explained qualitatively by the fact that in the benzo-2-pyrylocyanine series the carbon—carbon bonds of the pyrylium residues, owing to the tendency of the benzene rings annelated to them to retain their aromatic character, participate to a smaller extent in conjugation than in the series of corresponding dyes from mononuclear heterocycles.

Quantum-chemical calculations of the changes in the C—C bond orders (δ) [8] during electronic excitation by the Hückel molecular orbital (HMO) method [9] showed that the broadening of the absorption bands on passing from the 4-substituted to the 2-substituted isomers is due to intensification of the vibron interactions. For example, for dyes VIIIa,b the values calculated for the same values of the quantum-chemical parameters as in [8] are, respectively, 0.1887 and 0.1131. An analysis of the changes in the orders of the individual bonds showed that the significant decrease in the C_3—C_4 bond order during excitation makes the principal contribution to the overall δ value for the 2-substituted isomers.

In the examined series of dyes replacement of the oxygen atoms by sulfur atoms gives rise to approximately the same bathochromic shift of the absorption bands ($\Delta_{M^{-1}} \approx 90$ nm) as in the series of isomeric flavylocyanines. This replacement also leads to contraction of the bands, which is accompanied by a simultaneous decrease in the coefficients of asymmetry, excess, and the fine structure. Similar changes in the absorption spectra are produced by replacement of the oxygen atoms by sulfur atoms in the pyrylocyanine series [7].

It is interesting to note that the long-wave absorption band of 4,4'-diphenyl-substituted benzo-2-thiopyrylocyanine IXa has an unusual (for a symmetrical dye) form with an inflection on the long-wave branch.

In contrast to the corresponding γ isomers, contraction of the absorption bands not only on passing from monomethylidynecyanines to carbo- but also to dicarbocyanines is observed for the examined benzo-2-pyrylocyanines and their thio analogs. This constitutes evidence that the widths of the bands of these dyes are determined to a greater degree by a change in the vibron interaction than by the solvating effect of the solvent.

TABLE 3. Characteristics of the Synthesized Compounds

Compound	mp,[a] °C	Found, %		Empirical formula	Calculated, %		Yield, %
		Cl	S		Cl	S	
I	151—152	11,0		$C_{16}H_{13}ClO_5$	11,1		25
II	150—151	10,6	9,6	$C_{16}H_{13}ClO_4S$	10,6	9,5	36
VI	121—122	(77,3; 4,5)[b]	12,3	$C_{17}H_{12}OS$	(77,3; 4,6)[b]	12,1	89
VIIa	257	6,4		$C_{31}H_{21}ClO_6$	6,8		10
VIIIa	244—245	6,6	(71,4; 4,1)[b]	$C_{33}H_{23}ClO_6$	6,5	(71,9; 4,2)[b]	54
IXa	216	6,3		$C_{35}H_{25}ClO_6$	6,2		16
Xa	298—300	6,7	11,5	$C_{31}H_{21}ClO_4S_2$	6,4	11,5	34
XIa	261	5,9	10,6	$C_{33}H_{23}ClO_4S_2$	6,1	11,0	62
XIIa	150	5,9	10,2	$C_{35}H_{25}ClO_4S_2$	5,8	10,5	15
XIIIa	153—154	6,9		$C_{29}H_{26}ClNO_5$	7,1		46
XIVa	227—228	6,7	6,2	$C_{29}H_{26}ClNO_4S$	6,8	6,2	90
XVa	246—247	7,1	6,8	$C_{27}H_{22}ClNO_5S$	7,0	6,3	41
XVIa	258—259	6,7	12,4	$C_{27}H_{22}ClNO_4S_2$	6,7	12,2	25

[a] The compounds were crystallized: VI from aqueous alcohol, XIIa from $(Ac)_2O$, XVa from AcOH—$(Ac)_2O$ (2:1), XVIa from AcOH—$(Ac)_2O$ (1:1), and the remaining compounds from AcOH.

[b] The indexes of the percentages of C and H, respectively, are presented in parentheses.

The monomethylidynecyanines are not subject to all of the regularities noted above. Thus, in contrast to carbo- and dicarbocyanines, for the monomethylidynecyanines of the α series the extinctions and the coefficients of excess and the fine structure are higher than for the isomeric dyes of the γ series, which should be explained by the large steric hindrance in the molecules of the latter. Thiopyrylomonomethylidynecyanine Xa absorbs only 23 nm more deeply than its oxygen analog. In addition, an anomalously large difference ($\Delta\lambda$ = 182 nm, Δ_{M-1} = 176 nm) is observed between the absorption of this dye and its higher vinylog. A similar phenomenon, the possible reason for which is interaction of the unbonded sulfur atoms, was also observed in the α-thiopyrylocyanine [7] and isobenzothiopyrylocyanine [10] series.

A distinct conclusion regarding the decrease in the same sequence of the electron-donor character of the heterocyclic residues in the dyes follows from the increase in the deviations for the unsymmetrical dyes (Table 2) on passing from the compounds of the α series to the compounds of the γ series and from benzopyrylium derivatives to the benzothiopyrylium derivatives. The indicated dependence is manifested both for (benzopyrylo)(indo)cyanines XIII and XIV and for (benzopyrylo)(thia)cyanines XV and XVI, for which the deviations are greater as a consequence of the large electronic asymmetry. The existence for the examined dyes, in contrast to their pyrylium and thiopyrylium analogs [11], of the regularity noted above is probably associated with the smaller difference in the position of the absorption bands of the corresponding symmetrical dyes.

EXPERIMENTAL

The absorption spectra were determined with an SF-4A spectrophotometer and were processed as in [1]. The purity of the preparations was monitored by thin-layer chromatography (TLC) on Silufol UV-254 plates with elution by acetonitrile.

2-Methyl-4-phenylbenzopyrylium Perchlorate (I). A solution of 3 g (18.75 mmole) of 2-methylchromone was added dropwise with steady refluxing of the reaction mixture to a solution of phenylmagnesium bromide, prepared from 5.8 g (39 mmole) of bromobenzene, 0.88 g (36.7 mmole) of Mg turnings, and 14 ml of dry ether, after which the mixture was cooled with ice and treated with 17 ml of concentrated HCl. The mixture was filtered, 3 ml of 70% $HClO_4$ was added, and the mixture was diluted with 300 ml of ether. Trituration gave 1.5 g of the salt (Table 3).

2-Methyl-4-phenylbenzothiopyrylium Perchlorate (II). This compound was similarly obtained in the form of yellow needles.

4-Phenylbenzopyrylium Perchlorate (III). A solution of 2 g (13.7 mmole) of chromone in 7 ml of benzene was added dropwise to a solution of phenylmagnesium bromide, prepared from 0.53 g (22 mmole) of Mg, 2.8 ml (27 mmole) of bromobenzene, and 8.4 ml of dry ether, during which pronounced heating up of the reaction mixture was observed. The mixture was refluxed on a water bath for 2 h, after which it was cooled to 0°C and treated with 4 ml of 70% $HClO_4$ and 15 ml of acetic acid and diluted with ether until the mixture became turbid. It was then filtered to give 0.6 g of yellow crystals of the salt.

4-Phenylbenzothiopyrylium Perchlorate (IV). This compound was obtained from phenylmagnesium bromide, prepared from 0.88 g (36.7 mmole) of Mg and 5.8 g (39 mmole) of bromobenzene in 14 ml of ether, and 3 g (17 mmole) of thiochromone in 20 ml of benzene by a method similar to that used to prepare III. The oil that separated after the addition of ~4 ml of 70% $HClO_4$ was triturated with a large amount of ether. To separate the inorganic impurities the reaction product was dissolved in CH_2Cl_2, and the solution was filtered and evaporated to give 0.5 g of the salt.

2-Formylmethylene-4-phenylbenzothiopyran (VI). A mixture of 0.4 g (1.19 mmole) of salt II and 0.24 ml of dimethylformamide (DMF) was refluxed in 8 ml of acetic anhydride for 30 min, after which the mixture was filtered to give 0.26 g of shiny brown crystals with λ_{max} 474 and 492 nm (CH_2Cl_2). The dimethylaminovinyl derivative was saponified by adding a 2% aqueous solution of NaOH dropwise to a solution of the derivative in 6 ml of acetonitrile until the color changed to bright yellow. Filtration gave 0.16 g of VI.

2-[(4-Phenyl-1-benzopyran-2-ylidine)methyl]-4-phenyl-1-benzopyrylium Perchlorate (VIIa). A mixture of 0.16 g (0.5 mmole) of salt I and 0.155 g (0.5 mmole) of III with 0.08 g (1 mmole) of anhydrous sodium acetate was heated in 2 ml of acetic anhydride to 80-100°C for 15 min, after which it was filtered to give green needles of VIIa.

2-[3-(4-Phenylbenzopyran-2-ylidene)propen-1-yl]-4-phenylbenzopyrylium Perchlorate (VIIIa). A mixture of 0.32 g (1 mmole) of salt I, 0.5 ml of ethyl orthoformate, and 0.08 g (1 mmole) of anhydrous sodium acetate was heated in 4 ml of a mixture of acetic acid and acetic anhydride (1:1) for 2 min, after which it was filtered to give 0.15 g of green crystals of dye VIIIa.

2-[5-(4-Phenylbenzopyran-2-ylidene)penta-1,3-dienyl]-4-phenylbenzopyrylium Perchlorate (IXa). A solution of 0.032 g (1.24 mmole) of (3-phenylaminopropen-2-ylidene)ammonium chloride in 2 ml of acetic anhydride was refluxed for 2 min, after which 0.08 g (0.25 mmole) of salt I was added. After the latter dissolved, 0.04 g of anhydrous sodium acetate was added, and the mixture was heated to 100°C for 5 min, and the precipitated green crystals were removed by filtration.

2-[(4-Phenyl-1-benzo-2-thiopyranyl)methyl]-4-phenyl-1-benzothiopyrylium Perchlorate (Xa). This compound was obtained from 0.33 g (1 mmole) of salt II and 0.32 g (1 mmole) of IV by a method similar to that used to prepare VIIa.

2-[3-(4-Phenylbenzothiopyran-2-ylidene)propen-1-yl]-4-phenylbenzothiopyrylium Perchlorate (XIa). This compound was obtained from 0.336 g (1 mmole) of salt II and ethyl orthoformate by a method similar to that used to prepare VIIIa. The dye precipitated from the hot solution in the form of bronze crystals.

2-[5-(4-Phenylbenzothiopyran-2-ylidene)penta-1,3-dienyl]-4-phenylbenzothiopyrylium Perchlorate (XIIa). This compound was obtained from 0.178 g (0.5 mmole) of salt II and 0.065 g (0.25 mmole) of (3-phenylaminopropen-2-ylidene)ammonium chloride by a method similar to that used to prepare IXa. The precipitated crystals were removed by filtration and washed on the filter with acetic acid and ether.

1,3,3-Trimethyl-2-[3-(4-phenylbenzopyran-2-ylidene)propen-1-yl]-3H-indolium Perchlorate (XIIIa). A mixture of 0.16 g (0.5 mmole) of salt I was heated with 0.15 g (0.75 mmole) of 1,3,3-trimethyl-2-formylmethyleneindoline in 1 ml of a mixture of acetic acid and acetic anhydride (1:1) for 2 min, after which it was filtered to give 0.115 g of the dye.

1,3,3-Trimethyl-2-[3-(4-phenylbenzothiopyran-2-ylidene)propen-1-yl]-3H-indolium Perchlorate (XIVa). This compound was obtained from 0.17 g (0.5 mmole) of salt II and 0.15 g (0.75 mmole) of 1,3,3-trimethyl-2-formylmethyleneindoline by a method similar to that used to prepare XIIIa.

2-[3-(4-Phenylbenzopyran-2-ylidene)propen-1-yl]-3-ethylbenzothiazolium Perchlorate (XVa). 2-Formylmethylene-4-phenylbenzopyran (V) was obtained in 77% yield from salt I by a method similar to that used to prepare VI. A mixture of 0.117 g (0.33 mmole) of 2-methyl-3-ethylbenzothiazolium p-toluenesulfonate and 0.08 g (0.33 mmole) of V in 2 ml of acetic anhydride was refluxed for 2 min. The dye was precipitated from the reaction mixture by means of a saturated aqueous solution of sodium perchlorate.

2-[3-(4-Phenylbenzothiopyran-2-ylidene)propen-1-yl]-3-ethylbenzothiazolium Perchlorate (XVIa). This compound was obtained from 0.13 g (0.5 mmole) of VI and an equimolar amount of 2-methyl-3-ethylbenzothiazolium p-toluenesulfonate by a method similar to that used to prepare XVa.

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