reagent (in ether), obtained from 2.36 g (0.01 mole) of 1-bromomethyl-o-carborane and 0.26 g (0.011 mole) of magnesium, during which the pyrylium salt dissolved. The mixture was treated with a saturated aqueous solution of ammonium chloride, washed with water, and dried with $MgSO_4$. The solvent was removed, the residue was triturated with alcohol, and the resulting precipitate was removed by filtration to give 1.2 g (35%) of a product with mp 119-121°C (from nitromethane). IR spectrum: 2600 (B—H) and 1705 cm^{-1} (C═C). PMR spectrum: 1.02 [s, 18H, $(CH_3)_3C$], 4.45 (d, 2H, 3-H and 5-H), 2.97 (s, 1H, 4-H), 3.53 (s, 1H, CH_{carb}), and 2.15 (s, 2H, CH_2). Found, %: C 54.5; H 9.8; B 31.0. $C_{16}H_{34}B_{10}O$. Calculated, %: C 54.8; H 9.8; B 30.8.

<u>2,6-Di-tert-butyl-4-o-carboranylmethylpyrylium Perchlorate.</u> A 0.1-ml (0.001 mole) sample of 70% $HClO_4$ was added to 0.35 g (0.001 mole) of 2,6-di-tert-butyl-4-o-carboranylmethyl-4H-pyran in 5 ml of acetic anhydride, and the reaction mixture was heated to the boiling point. It was then cooled and diluted with a large volume of ether, and the resulting precipitate was removed by filtration to give 0.11 g (25%) of a product with mp 255°C (from glacial acetic acid). IR spectrum: 2600 (B—H); 1630 and 1540 (pyrylium cation); 1100 cm^{-1} (ClO_4^-). Found, % B 24.3. $C_{16}H_{33}B_{10}ClO_5$. Calculated, %: B 24.1.

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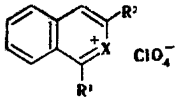
PYRYLOCYANINES. 9.* ISOBENZOPYRYLOCYANINES

A. I. Tolmachev and L. M. Shulezhko

UDC 547.814.5:541.651:668.819

Polymethine dyes with symmetrical and unsymmetrical structures, viz., 3-phenyl-2-benzopyrylium derivatives, were synthesized. Their colors are discussed.

Polymethine dyes that contain a 2-benzopyrylium ring were unknown up until now. Within our plan to investigate the dependence of the color on the chemical structure in the pyrylocyanine series, it seemed of interest to synthesize isomeric flavylocyanine [2, 3] dyes that contain 3- and 1-phenyl-substituted 2-benzopyrylium residues. In the synthesis of dyes of the first type we started from 1-methyl-3-phenyl-2-benzopyrylium perchlorate (Ia) or 1-formylmethylene-3-phenyl-2-benzopyran (III). Oxonium salt Ia was obtained by the action of methylmagnesium iodide on 3-phenylisocoumarin.



I a-c

I a X=O, $R^1=CH_3$, $R^2=C_6H_5$; b X=O, $R^1=C_6H_5$, $R^2=CH_3$; c $X=NCH_3$, $R^1=C_6H_5$, $R^2=CH_3$

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*See [1] for communication 8.

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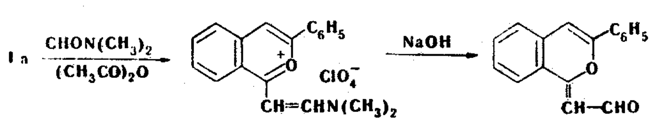
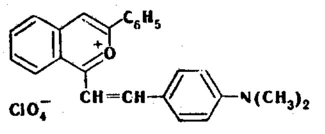
Aldehyde III was synthesized from salt Ia via the scheme:



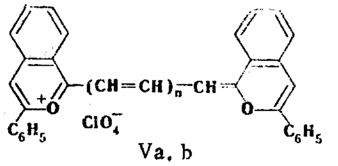
II III

Styryl IV was obtained by condensation of isobenzopyrylium salt Ia with p-dimethylaminobenzaldehyde in acetic anhydride, while symmetrical and unsymmetrical monomethylidynecyanines Va and VIa, respectively, were obtained by reaction in the same solvent with 3-phenyl-2-benzopyran-1-thione or 2-phenyl-1-benzopyran-4-thione. We were unable to obtain symmetrical isobenzopyrylotrimethylidynecyanine Vb by reaction of salt Ia with ethyl orthoformate. This dye was synthesized by stepwise condensation of 2-moles of salt Ia with ethylisoformanilide. An attempt to obtain unsymmetrical trimethylidynecyanines VIb, VII, and VIII by condensation of the same salt with anilinovinyl derivatives of flavylium, 1,3,3,-trimethyl(3H)indolium, and 3-methylbenzothiazolium salts was unsuccessful. We obtained the desired result by condensation of aldehyde III with the methyl-substituted derivatives of the corresponding heterocyclic salts.

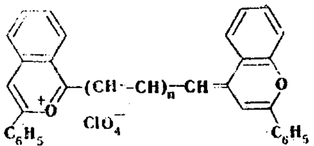


IV

λ_{max} 678nm (688)†, lg ε 5,11 (inCH_2Cl_2)

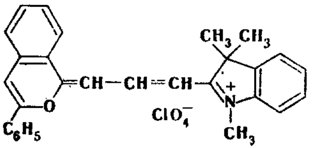


Va, b

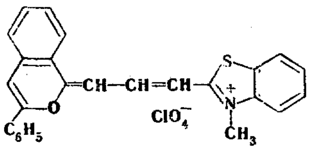


VI a,b

a n=0; b n=1



VII



VIII

Alcohol solutions of symmetrical isobenzopyrylocyanines, like many other pyrylocyanines, are unstable, while solutions of these dyes in glacial acetic acid, nitromethane, chloroform, and methylene chloride are relatively stable. Trimethylidynecyanine Vb becomes colorless when it is dissolved in trifluoroacetic acid as a consequence of protonation, while the addition of 70% perchloric acid is required for complete conversion of monomethylidynecyanine Va to the dication. Treatment of solutions of the isobenzopyrylocyanines in dimethylformamide (DMF) with methylamine is accompanied by disappearance of their absorption with the simultaneous appearance of bands in the shorter-wave region. This indicates the fundamental possibility of conversion of the dyes under consideration to their isoquinoline analogs.

The long-wave bands of the electron absorption spectra of solutions of unsymmetrical carbocyanines VIb, VII, and VIII in methylene chloride are presented in Fig. 1. It is apparent from the forms of the bands that, as in the case of other pyrylocyanines [4], the ratio of the intensities of the 0→0* transition to the intensities of the transitions to the vibrational sublevels decreases as the electronic asymmetry of the 2-benzopyrylotrimethylidynecyanines, which changes in the order VIb < VII < VIII, increases. The absorption curve of symmetrical isobenzopyrylotrimethylidinecyanine Vb has the form that is normal for symmetrical polymethine dyes.

The maxima and the logarithms of the molar extinctions, as well as the average position determined by the ratio of the zero and first moments (M^{-1}) [7], are presented in Table 1

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†For the flavylium analog.

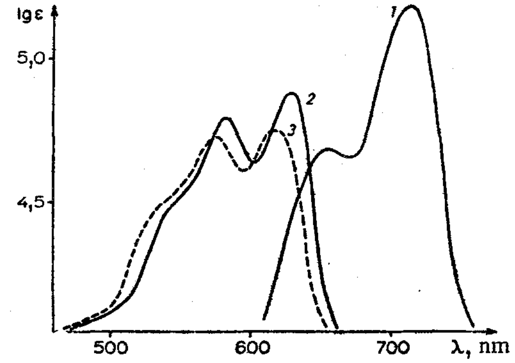

Fig. 1. Absorption spectra: 1) carbocyanine VIb; 2) carbocyanine VII; 3) carbocyanine VIII.

TABLE 1. Characteristics of the Long-Wave Absorption Bands of Solutions of Isobenzopyrylocyanines in Methylene Chloride

Compound	λ_{max}, nm	lg ε	M^{-1}, nm	D_λ,* nm	$D_{M^{-1}}$, nm
Va	596 (602)†	4.57 (4,88)	563,0 (586,4)	—	—
Vb	707 (716)	5,02 —	674,7 (695,9)	—	—
VIa	588 —	4,70 —	564,9 —	—	—
VIb	712 —	5,20 —	684,9 —	0	0,4
VII	582, 625 (595, 640)	4,76; 4,83 (4,69; 4.66)	579,7 (586,8)	—	20,6 (24,1)
VIII	574, 616 (585, 627)	4,72; 4,74 (4,81; 4,76)	568,6 (573,9)	—	40,6 (46,0)

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*The λ_{max} (M^{-1}) values of solutions of symmetrical inda- and thiatrimethylidynecyanines in methylene chloride used for the calculation of D_λ and $D_{M^{-1}}$ are, respectively, 550 (526.0) and 562 (543.8) nm.

†The same characteristics of the analogous flavylocyanines are presented in parentheses. An analog of dye VII was described in [5], and an analog of dye VIII are described in [6], in which it was erroneously presented as the N-ethyl derivative.

for the long-wave absorption bands of the dyes obtained. The deviations (D and $D_{M^{-1}}$) [8] determined as the deviations of the λ_{max} or M^{-1} values from the half-sums of the analogous characteristics of symmetrical dyes constructed from the same heterocyclic residues are also presented for unsymmetrical trimethylidynecyanines in Table 1. We used the method of deviations to estimate the electron-donor character (the relative "basicity") of the examined oxygen-containing heteroring in the dyes. As in a number of other cases (for example, [4]), in view of the pronounced difference in the forms of the absorption curves of the symmetrical and unsymmetrical dyes, this kind of estimate with the aid of the moments of the bands is more accurate.

All of the synthesized isobenzopyrylocyanines with both symmetrical (Va, b) and unsymmetrical (IV, VII, and VIII) structures absorb somewhat higher than the isomeric flavylocyanines, and the difference in the average positions of the bands (M^{-1}) is greater than the difference in the absorption maxima. A quantum-chemical calculation of the molecules of symmetrical trimethylidynecyanine Vb (M^{-1}_{calc} 619 nm) and its flavylium analog (M^{-1}_{calc} 687 nm) also leads to the qualitative conclusion that isobenzopyrylocyanines have colors with higher wavelengths. Let us note that the observed difference in the absorption of isobenzopyrylo- and flavylocyanines is relatively small, although a quantum-chemical estimate leads to a considerably smaller effective length [9] of the 3-phenylisobenzopyrylium ring (4.17) as compared with the flavylium ring (5.83). It is apparent from a comparison of the spectral characteristics of symmetrical dyes Va, b that the first vinylene shift of the long-wave absorption band is close to 100 nm in the 2-benzopyrylo-1-cyanine series, which indicates the absence of substantial steric hindrance in the cation of monomethylidynecyanine Va. From an examination of the characteristics of unsymmetrical carbocyanines it is apparent that deviation in the case of dye VIb, which is made up of isobenzopyrylium and flavylium residues, is actually absent, and this indicates that these heterorings have similar electron-donor character. In contrast to carbocyanine VIb, in the case of dyes VII and VIII one observes significant deviations, which, however, are somewhat lower than for the isomeric dyes that contain a flavylium residue in place of 3-phenyl-2-benzopyrylium residues. The latter regularity is also displayed in the case of nitromethane solutions (for which the $D_{M^{-1}}$ values for dyes VII and VIII and their flavylium analogs are, respectively, 31, 60.8, 35.2, and 67.6 nm). These facts make it possible to conclude that the "basicity" of the heteroring under consideration is somewhat higher in polymethine dyes than the "basicity" of the isomeric system that contains an oxygen atom in the 1 position.

In contrast to the dyes that contain a 3-phenyl-2-benzopyrylium ring attached to the polymethine chain in the 1 position, we were unable to obtain isomeric compounds with 1-phenyl-2-benzopyrylium ring attached to the 3 position. 1-Phenyl-3-methyl-2-benzopyrylium perchlorate (Ib), which was synthesized in the present research and is readily converted to isoquinolinium salt Ic by reaction with methylamine, in contrast to Ia, does not undergo cyanine condensation. Salt Ib, like its 6,7-dimethoxy analog [10], does not react even with aromatic aldehydes. We were also unable to condense 1-phenyl-2,3-dimethylisoquinolinium perchlorate (Ic) with p-dimethylaminobenzaldehyde, despite the data in [11], according to which the 3-methylisoquinolinium salt does undergo this sort of condensation.

EXPERIMENTAL

The electronic absorption spectra of 1- and 5-cm thick layers of $8 \cdot 10^{-6}$ to $2 \cdot 10^{-5}$ mole/liter solutions of the compounds were recorded with an SF-4A spectrophotometer as in [7]. The mathematical treatment of the absorption spectra was accomplished with the program in [12]. The PMR spectra of 0.1 M solutions of the compounds in CF_3COOH were recorded with a Tesla BS-487-B spectrometer (80 MHz) at 20°C with tetramethylsilane as the internal standard. The quantum-chemical calculations were made with an ÉLA program [13] with the following parameters: $\alpha_O = \alpha_C + 2\beta$, $\beta_{CO} = 0.7\beta$ [14], and $\beta_{C-Ph} = 0.8\beta$.

The purity of the preparations was monitored by thin-layer chromatography (TLC). Chromatography was carried out on places with a fixed layer of Silufol-254 silica gel (elution with acetonitrile).

1-Methyl-3-phenyl-2-benzopyrylium Perchlorate (Ia). A solution of methylmagnesium iodide, obtained from 0.6 g (0.025 g-atom) of magnesium and 3.55 g (25 mmole) of methyl iodide in 15 ml of ether, was added at 0°C to a suspension of 4.66 g (21 mmole) of 3-phenylisocoumarin [15] in 20 ml of ether, and the mixture was stirred at room temperature for 5 h. It was then treated with 12 g of ammonium chloride in 70 ml of water, and the ether layer was separated, washed with water, and dried with calcium chloride. A mixture obtained by dropwise addition of 4 ml of 70% perchloric acid to 16 ml of acetic anhydride at 0°C was added, and the precipitate was removed by filtration and washed with ether. PMR spectrum: 3.65 (3H, s, CH_3) and 7.57-8.75 ppm (10H, m, aromatic protons) (Table 2).

1-Phenyl-3-methyl-2-benzopyrylium Perchlorate (Ib). A solution of phenylmagnesium bromide, obtained from 0.36 g (0.015 g-atom) of magnesium and 2.35 g (15 mmole) of bromobenzene in 10 ml of ether, was added with stirring at 0°C to a suspension of 1.6 g (10 mmole) of 3-methylisocoumarin [16] in 15 ml of dry ether, after which the reaction was carried out as the preparation of Ia. Workup gave the product in 30% yield. PMR spectrum: 3.05 (3H, s, CH_3) and 7.75-8.75 ppm (10H, m, aromatic protons). The product was also identified by conversion to 1-phenyl-2,3-dimethylisoquinolinium perchlorate (Ic), for which a mixture of 0.5 g (1.5 mmole) of Ib, 5 ml of acetone, and 0.5 ml of a 19% aqueous solution of methylamine was heated on a boiling-water bath for 5 min. The solution was evaporated in vacuo (with a water aspirator), and the precipitate was removed by filtration and washed with water, alcohol, and ether.

1-(2-Dimethylaminovinyl)-3-phenyl-2-benzopyrylium Perchlorate (II). A solution of 0.96 g (3 mmole) of salt Ia in 3 ml of DMF and 15 ml of acetic anhydride was heated to the boiling point, after which it was cooled, and the reaction product was removed by filtration.

1-Formylmethylene-3-phenyl-2-benzopyran (III). A 0.21-g (0.56 mmole) sample of salt II was shaken at room temperature for 1 h in a mixture of 9 ml of acetonitrile and 12 ml of a 12% aqueous solution of sodium hydroxide, after which the precipitate was removed by filtration, and the filtrate was diluted with water. The precipitate was again removed by

TABLE 2. Characteristics of the Synthesized Compounds

Compound	mp, °C*	Found, %					Empirical formula	Calc., %					Yield, %
		C	H	Cl	N	S		C	H	Cl	N	S	
Ia	192	59,9	4,0	11,1	—	—	$C_{16}H_{13}ClO_5$	59,9	4,0	11,1	—	—	37
Ic	260	—	—	10,5	4,2		$C_{17}H_{16}ClNO_4$	—	—	10,6	4,2		41
II	272			9,6	3,8		$C_{19}H_{18}ClNO_5$	—	—	9,5	3,7	—	19
III	129	81,9	5,1	—	—	—	$C_{17}H_{12}O_2$	82,3	4,8	—	—	—	79
IV	219	—	—	7,7	—	—	$C_{25}H_{22}ClNO_5$	—	—	8,0	—	—	14
Va	260	70,9	4,0	6,7	—	—	$C_{31}H_{21}ClO_6$	70,9	4.0	6,8	—	—	64
Vb	270	—	—	6,2	—	—	$C_{33}H_{23}ClO_6$	—	—	6,4	—	—	15
VIa	270	70,9	4,1	6,5	—	—	$C_{31}H_{21}ClO_6$	70,9	4,0	6,8	—	—	66
VIb	286	71,8	4,2	6,3	—	—	$C_{33}H_{23}ClO_6$	71,9	4,2	6,5	—	—	79
VII	262	—	—	7,1	3,1	—	$C_{29}H_{26}ClNO_5$	—	—	7,1	2,8	—	44
VIII	268	—	—	7,3	—	6,3	$C_{26}H_{20}ClNO_5S$	—	—	7,2	—	6,5	28

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*The compounds were crystallized: Ic from alcohol, II, Va, and VII from acetic acid, III from water–alcohol (1:1), Vb from acetic anhydride, and VIII from acetic acid–acetic anhydride (4:1).

filtration and washed with water.

1-(p-Dimethylaminostyryl)-3-phenyl-2-benzopyrylium Perchlorate (IV). This compound was obtained from 0.3 mmole of salt Ia and 0.3 mmole of p-dimethylaminobenzaldehyde in acetic anhydride by heating to the boiling point for 2 min. It was purified by washing with glacial acetic acid and ether.

1-[3-(3-Phenyl-2-benzo-1-pyranylidene)methyl]-3-phenyl-2-benzopyrylium Perchlorate (Va). This compound was obtained from 0.3 mmole of salt Ia and 0.33 mmole of 3-phenyl-1-thioisocoumarin [17] by the method used for the synthesis of IV. The dye was precipitated with ether.

1-[(3-Phenyl-2-benzo-1-pyranylidene)propene-1-yl]-3-phenyl-2-benzopyrylium Perchlorate (Vb). A mixture of 0.16 g (0.5 mmole) of salt Ia and 0.149 g (0.5 mmole) of ethylisoformanilide in a mixture of 3.4 ml of acetic anhydride and 1.6 of glacial acetic acid was refluxed for 2 min, after which it was cooled and treated with 0.16 g of Ia and 0.04 g of anhydrous sodium acetate, and the mixture was heated to the boiling point. The dye was removed by filtration and washed with acetic acid and ether.

1-[(2-Phenyl-1-benzo-4-pyranylidene)methyl]-3-phenyl-2-benzopyrylium Perchlorate (VIa). This compound was obtained from 0.05 mmole of salt Ia and 0.6 mmole of 4-thioflavone as in the preparation of IV, except that the mixture was refluxed for 5 min. The product was purified by reprecipitation from a solution in acetonitrile by the addition of ether.

1-[3-(2-Phenyl-1-benzo-4-pyranylidene)prop-1-en-1-yl]-3-phenyl-2-benzopyrylium Perchlorate (VIb). This compound was obtained from 0.08 mmole of aldehyde III and 0.08 mole of 4-methylflavylium perchlorate by the method used to prepare VIa and was isolated as in the preparation of IV.

1,3,3-Trimethyl-2-[3-(3-phenyl-2-benzo-1-pyranylidene)prop-1-en-1-yl]-3H-indolium Perchlorate (VII). This compound was obtained from 0.3 mmole of aldehyde III, 0.3 mmole of 1,2,3,3-tetramethyl-3H-indolium perchlorate, and 0.025 g of anhydrous sodium acetate in a mixture of 1.5 ml of acetic anhydride and 1 ml of acetic acid by refluxing for 5 min and was isolated as in the preparation of IV.

1-Methyl-2-[3-(3-phenyl-2-benzo-1-pyranylidene)prop-1-en-1-yl]benzothiazolium Perchlorate (VIII). This compound was obtained from 0.3 mmole of aldehyde III, 0.305 mmole of 2,3-dimethylbenzothiazolium methylsulfate, 0.025 g of anhydrous sodium acetate, and 0.045 g of anhydrous sodium perchlorate in 2 ml of a mixture (1:1) of acetic acid and acetic anhydride by heating to the boiling point.

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CONDENSED HETEROCYCLES. 39.* QUANTUM-CHEMICAL CALCULATIONS OF THE REACTIVITIES OF SOME CONDENSED SULFUR AND SELENIUM HETEROCYCLES

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and Ya. L. Gol'dfarb

UDC 547.737'739.3:541.67

A number of isomeric thienothiophenes, selenophenothiophenes, and selenophenoselenophenes, as well as their C-protonated forms (σ complexes), were calculated by the self-consistent-field (SCF) MO LCAO method with the CNDO/2 approximation and the spd basis. Their reactivities in electrophilic substitution reactions were investigated theoretically by means of the localization energy approach. The results were compared with the available experimental data. The dependence of the specificity of electrophilic attack on the size of the attacking reagent was investigated for compounds with various heteroatoms. It is shown that the reactivity of the α position relative to the selenium atom should increase as the size of the attacking reagent increases.

The specific characteristics of the chemical behavior of a heteroaromatic compound are known to be due to the presence in the molecule of a heteroatom, which is not only a "supplier" of electrons for the formation of an aromatic π-electron structure but also an orienter that determines the specificity of attack by electrophilic or nucleophilic agents. The picture is complicated when one examines condensed systems. In this case not only the type of condensation (the mutual orientation of the heteroatoms) but also the electronic effects due to the nature of the heteroatoms have a considerable effect on the physical properties and reactivities of the compounds. Condensed heteroaromatic systems, particularly those that include different heterocycles, are therefore interesting subjects for the study of the effect

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*See [1] for communication 38.

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