PYRYLOCYANINES.

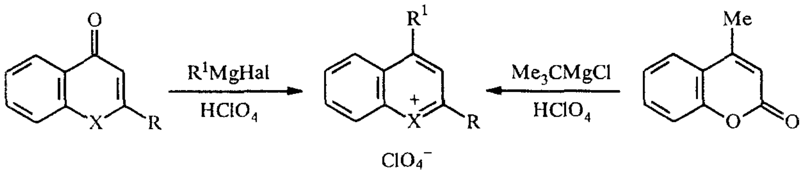
29.* tert-BUTYL-SUBSTITUTED BENZOPYRYLOCYANINES

M. A. Kudinova, V. V. Kurdyukov,
A. A. Ishchenko, and A. I. Tolmachev

2-tert-Butyl-4-methyl- and 2-methyl-4-tert-butylbenzopyrylium salts, as well as the sulfur analog of the latter, were synthesized. Polymethine dyes with symmetrical and unsymmetrical structures were obtained from these salts. The factors that affect the color are analyzed.

It is known that 2-phenyl-4-benzopyrylocyanines (flavylocyanines) are somewhat more highly colored than the isomeric 4-phenyl-2-benzopyrylocyanines [2]. On the other hand, in series of cyanines that contain 2,6- or 4,6-diphenylpyrylium residues the dyes of the α series are more deeply colored (by 110-150 nm) than those of the γ series [3]. This difference may be due to the different degree of participation in the overall conjugation system of, on the one hand, the carbon—carbon bonds of the α-pyrylium and α-benzopyrylium residues and, on the other, the phenyl groups in the 2 and 4 positions of these residues. Thus to ascertain the effect of the addition to the polymethine chromophore of benzopyrylium residues in the 2 or 4 positions on the color isomeric benzopyrylocyanines that do not contain phenyl substituents should have been examined. It is not possible to obtain 2-unsubstituted 4-benzopyrylocyanines because of the high electrophilicity of the 2 position in benzopyrylium salts. To solve the problem posed above we therefore obtained tert-butyl-substituted 2-benzopyrylo- and 4-benzopyrylocyanines. The indicated dyes are also of interest in connection with the fact that some pyrylocyanines that contain precisely these substituents are finding application for the solution of a number of practical problems associated with the transformation of light energy [4].

To obtain di-tert-butyl-substituted dyes we synthesized 4-methyl-2-tert-butyl- and 2-methyl-4-tert-butylbenzopyrylium salts IIa, b and the sulfur analog (IIc) of the latter. Salt IIa was obtained by treatment of 2-tert-butylchromone (Ia) with methylmagnesium iodide. It was found that it can be synthesized even more simply by the action of tert-butylmagnesium chloride on 4-methylcoumarin, although it is known that 2,2-dialkyl(aryl)-2H-benzopyrans are formed when it is treated with n-alkyl(aryl)magnesium halides [5]. Salts IIb, c were obtained by the action of the same reagent on 2-methylchromone and 2-methylthiochromone.



Ia-c

II a-c

Ia R=C(CH$_3$)$_3$, X=O; b R=CH$_3$, X=O; c R=CH$_3$, X=S; IIa R=C(CH$_3$)$_3$, R^1=CH$_3$, X=O;
b R=CH$_3$, R^1=C(CH$_3$)$_3$, X=O; c R=CH$_3$, R^1=C(CH$_3$)$_3$, X=S

The methyl groups in the synthesized onium salts are active with respect to electrophilic reagents; this was used for the synthesis of polymethine dyes from them. The condensation of salt IIa with 2-tert-butyl-4-thiochromone gave monomethylidynecyanine IIIa. The reaction of salts IIa-c with ethyl orthoformate or with [(3-phenylamino)-2-propen-1-

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*See [1] for Communication 28.

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TABLE 1. Characteristics of the Synthesized Compounds

Compound	Empirical formula	mp,* °C	Yield, %
IIa	$C_{14}H_{17}ClO_5$	220...222	60**
II b	$C_{14}H_{17}ClO_5$	217...218	44
IIc	$C_{14}H_{17}ClO_4S$	214...215	20
IIIa	$C_{27}H_{29}ClO_6$	302...304	85
III b	$C_{29}H_{31}ClO_6$	330...334	64
III c	$C_{31}H_{33}ClO_6$	241...244	78
IVa	$C_{29}H_{31}ClO_6$	248...250	70
IV b	$C_{31}H_{33}ClO_6$	133...135	90
IV c	$C_{29}H_{31}ClO_4S_2$	159...162	23
IV d	$C_{31}H_{33}ClO_4S_2$	215...216	38
Va	$C_{27}H_{30}ClNO_5$	208...210	75
V b	$C_{23}H_{26}ClNO_5$	262...264	100
VIa	$C_{27}H_{30}ClNO_5$	115...118	60
VI b	$C_{23}H_{26}ClNO_5$	223...225	83
VI c	$C_{27}H_{30}ClNO_4S$	114...115	98
VI d	$C_{23}H_{26}ClNO_4S$	230...232	95
VII	$C_{21}H_{15}ClO_6$	202...205	26

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*The compounds were crystallized: IIa-c, IVa, and VIa, c, d from acetic acid, IIIa-c, Vb, VIb, and VII from acetonitrile, IVa, c from tert-butyl alcohol—acetonitrile (2:1), and Va from ethanol—ether (2:1).

**By method A.

TABLE 2. Characteristics of the Long-Wave Absorption Bands of Solutions of Dyes III-VI in Methylene Chloride

Dye	λ_{max}, nm	lg ε	M^{-1}, nm	Dye	λ_{max}, nm	lg ε	M^{-1}, nm	D_λ, nm	$D_{M^{-1}}$, nm
III a	550	4,94	542,1	V a	576,616	4,86; 4,88	572,8	-8,5	15,3
III b	665	5,46	647,9	V b	660	5,07	639,4	-21,5	-15,5
III c	775	5,51	752,1	VI a	590,636	4,84; 4,76	574,9	19	11,1
IV a	626,684	4,78; 5,15	645,3	VI b	670	4,99	636,6	-22	-14,0
IV b	710,786	4,78; 5,24	746,9	VI c	638,688	4,80; 4,71	623,5	17	13,7
IV c	767,792	4,99; 4,99	748,5	VI d	700	4,92	689,7	2	-15,5
IV d	892	5.18	849.6						

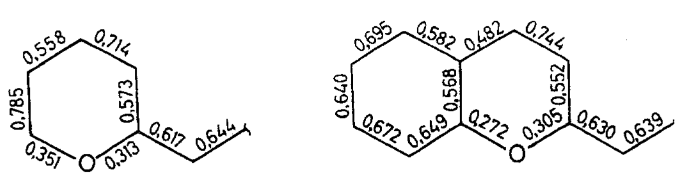
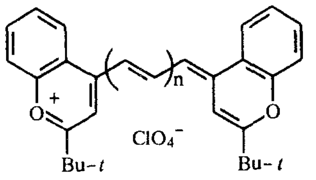
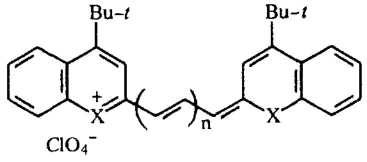


Fig. 1. Orders of the π bonds in the ground state of symmetrical 2-pyrylo- and 2-benzopyrylocarbocyanines.

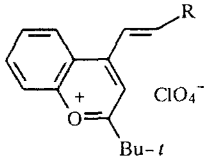
ylidene]phenylammonium chloride gave, respectively, trimethylidynecyanines IIIb and IVa, c or pentamethylidynecyanines IIIc and IVb, d. The condensation of salts IIa-c with 1,3,3-trimethyl-2-formylmethyleneindoline or with p-dimethylaminobenzaldehyde was also used to synthesize unsymmetrical (indo)(benzopyrylo)trimethylidynecyanines Va and VIa, c and styryl dyes Vb and VIb, d. The characteristics of the synthesized dyes are presented in Table 1.



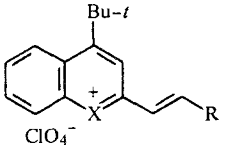
III a-c



IVa-d

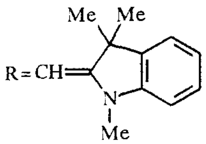


Va,b



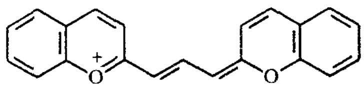
VI a-d

Va VI



III a $n=0$, b $n=1$, c $n=2$; IVa $n=1$, X=O; b $n=2$, X=O; c $n=1$, X=S, d $n=2$, X=S; VIa, b X=O, c, d X=S;
Vb, VIb, d $R=C_6H_4NMe_2\text{-}4$

4-Unsubstituted 2-benzopyrylotrimethylidynecyanine VII was synthesized by the action of ethyl orthoformate on 2-methylbenzopyrylium tetrachloroferrate with subsequent treatment with 20% perchloric acid.



VII

λ_{max}, nm (lg ε) = 687 (5,10) in CH_2Cl_2

In addition to the λ_{max} and log ε values, as in [2], the mean positions of the absorption bands M^{-1} determined by the method of moments are presented in Table 2 for solutions of the synthesized dyes in methylene chloride. The M^{-1} values for 4-benzopyrylocyanines IIIa-c are located in a shorter-wave region (by ≈45 nm) than in the case of their 2-phenyl-substituted analogs (see Table 2 and [2]). The analogous difference in series of 2-benzopyrylocyanines is 29 nm, while for the sulfur-containing analogs of the latter (IVc, d) it decreases to 10.5 and 13.1 nm, respectively. The same principles are also observed in the λ_{max} values of the long-wave absorption bands of these dyes.

It follows from the information stated above that the auxochromic effect of a phenyl substituent in the 2 position of the benzopyrylium residue is greater than that of a phenyl substituent in the 4 position; in the latter case it decreases when the oxygen atom in the heteroring is replaced by a sulfur atom. As a result, in contrast to phenyl-substituted benzopyrylocyanines, among which the 2-substituted isomers are, as already noted above, somewhat more highly colored than the 4-substituted isomers, the opposite principle is observed for the location of the absorption maxima in a series of their tert-butyl-substituted analogs. The locations of the M^{-1} band moments differ little for the isomeric compounds. The above-noted principle is probably associated with an increase in the torsion angle between the planes of the heteroring and the phenyl substituents in the order 2-phenylbenzopyrylium < 4-phenylbenzopyrylium < 4-phenylbenzothiopyrylium under the influence of the steric hindrance of the 4-phenyl group on the part of the hydrogen atom in the 5 position of the benzopyrylium fragment.

Thus the direction of the change in the color between tert-butyl-substituted benzopyrylocyanines is the same as for tert-butyl-substituted pyrylocyanines; however, the effect is smaller by a factor of three to five in absolute value [6].

The difference in the color of the isomeric dyes cannot be determined by the difference in the electronic effect of the tert-butyl group in the 2 and 4 positions of the benzopyrylium rings. Quantum-chemical calculations show that for dyes of the γ series this group should give rise to a hypsochromic shift of ≈3 nm, as compared with ≈5 nm for dyes of the α series. This small effect of the tert-butyl group is confirmed experimentally. In fact, the hypsochromic shift of λ_{max} on passing from unsubstituted 2-benzopyrylotrimethylidynecyanine VII to its 4,4'-di-tert-butyl-substituted analog IVa reaches only 3 nm, while the color of the isomeric dyes IIIb and IVa differs by 19 nm.

It is apparent from the results of quantum-chemical calculations of the bond orders that for pyrylo-2-cyanines the C—O bonds approach single bonds to a considerable degree (Fig. 1), as a consequence of which the heteroatom is weakly conjugated with the polymethine chromophore. However, this leads to greater participation of the carbon—carbon bonds of the heteroresidue in the overall conjugation system. The 2-pyrylocyanines and their heteroanalogs are therefore more deeply colored than their 4-substituted isomers. Annelation along the $C_{(5)}$—$C_{(6)}$ bond in dyes of the α series decreases the orders of the C—O bonds to an even greater extent (see Fig. 1). This should have led to an increase in the participation of the carbon—carbon bonds of the heteroresidue in the overall conjugation system. However, this sort of annelation also sharply decreases the orders of other bonds of the pyran residue in addition to the $C_{(3)}$—$C_{(4)}$ bond. The order of the $C_{(5)}$—$C_{(6)}$ bond undergoes a particularly substantial decrease. As a result of this, the participation of the carbon—carbon bonds of the heteroresidue in the overall conjugation system is weakened. The difference in the color of the isomeric tert-butyl-substituted benzopyrylocyanines is therefore substantially smaller than in the case of their mononuclear analogs.

Deviations D_{M-1} of styryl dyes Vb and VIb, d calculated from the band moments have negative values that are close in absolute value. One cannot draw definite conclusions regarding the electron-donor character of the heterocyclic residues on the basis of these values. On the other hand, it follows from a comparison of the deviations of unsymmetrical (indo)(benzopyrylo)trimethylidynecyanines Va and VIa, c that the same principle as that observed for the phenyl-substituted dyes is observed for the tert-butyl-substituted dyes. The deviations increase on passing from a compound of the α series (VIa) to its isomer of the γ series (Va) and from benzopyrylium derivative VIa to its sulfur-containing analog VIc. This is in agreement with the conclusion that the electron-donor character of the heterocyclic residues decreases in the same order [2]. In addition, the D_{M-1} values themselves are smaller for the examined dyes than for their phenyl-substituted analogs; this is due to the increase in the electron-donor character of the residues under the influence of replacement of the electron-acceptor phenyl substituents by tert-butyl groups, which have a positive inductive effect. The indicated difference for γ-isomer Va (8.9 nm) is greater than for the compounds of the α series VIa, c (0.5 and 2.5 nm). This is in agreement with the greater effect of phenyl groups in the 2 position on the properties of the dyes from the examined heterocycles than the effect of phenyl groups in the 4 position.

EXPERIMENTAL

The absorption spectra of solutions of II-VII in methylene chloride stabilized with 1% absolute ethanol were recorded with a Specord M-40 spectrophotometer. The purity of the preparations was monitored by TLC on Silufol UV-254 plates with elution by acetonitrile. The PMR spectra of solutions in d_3-acetonitrile were obtained with a Bruker WP-200 spectrometer (at 200 and 132 MHz) at 25°C with hexamethyldisiloxane (HMDS) as the internal standard. The quantum-chemical calculations were carried out by the Hückel molecular orbital (HMO) method with the same parameters as those in [6].

The results of elementary analysis for C, H, Cl, and S were in agreement with the calculated values.

2-tert-Butyl-4-methylbenzopyrylium Perchlorate (IIa). A. A solution of a Grignard reagent obtained from 0.96 g (0.04 g-atom) of magnesium and 5.8 g (0.04 mole) of methyl iodide in 50 ml of ether was added dropwise to a solution of 4 g (0.02 g) of 2-tert-butyl-4H-benzopyran-4-one (Ia) in 40 ml of absolute ether, and the reaction mixture was refluxed for 40 min. The bulk of the ether was removed in vacuo, and 100 ml of 20% perchloric acid was added with cooling. The salt was removed by filtration and washed with water and ether. UV spectrum, λ_{max} (log ε): 246 (4.35), 330 nm (4.21). PMR spectrum, δ: 1.69 [9H, s, $C(CH_3)_3$], 3.08 (3H, s, CH_3), 8.14-8.52 ppm (5H, m, Ar—H).

B. A solution of a Grignard reagent obtained from 0.55 g (0.022 g-atom) of magnesium and 1.9 g (0.02 mole) of tert-butyl chloride in 6 ml of ether was added dropwise to a solution of 1 g (0.006 mole) of 4-methylcoumarin in 15 ml of dry benzene, and the reaction mixture was refluxed for 30 min. The bulk of the solvents was removed in vacuo, and 50 ml of 20% perchloric acid was added with cooling. The salt was removed by filtration and washed with water and ether.

2-Methyl-4-tert-butylbenzopyrylium and 2-Methyl-4-tert-butylbenzothiopyrylium Perchlorates (IIb, c). These salts were synthesized in the same way as IIa (method B) starting from Ib, c. **Compound IIb**: UV spectrum, λ_{max} (log ε): 247 (4.25), 332 nm (4.01). PMR spectrum, δ: 1.64 [9H, s, $C(CH_3)_3$], 3.10 (3H, s, CH_3), 7.90-8.74 ppm (5H, m, Ar—H). **Compound IIc**: UV spectrum, λ_{max} (log ε): 265 (4.21), 342 (3.54), 385 nm (3.30). PMR spectrum, δ: 1.72 [9H, s, $C(CH_3)_3$], 3.20 (3H, s, CH_3), 8.11-9.14 ppm (5H, m, Ar—H).

2-tert-Butyl-4-[(2-tert-butylbenzopyran-4-ylidene)methyl]benzopyrylium Perchlorate (IIIa). A mixture of 0.3 g (1 mmole) of salt IIa and 0.22 g (1 mmole) of 2-tert-butyl-4H-benzopyran-4-thione in 4 ml of acetic anhydride was heated at 120°C for 30 min, after which the dye was removed by filtration and washed with benzene and ether.

2-tert-Butyl-4-[3-(2-tert-butylbenzopyran-4-ylidene)-1-propen-1-yl]benzopyrylium Perchlorate (IIIb). A mixture of 0.3 g (1 mmole) of salt IIa, 0.148 g (1 mmole) of ethyl orthoformate, and 0.082 g (1 mmole) of anhydrous sodium acetate in 3 ml of a mixture of acetic anhydride with acetic acid (1:1) was heated at 120°C for 20 min, after which the dye was removed by filtration, washed with ether, and chromatographed on Al_2O_3 by elution with acetonitrile—acetic acid (1:1). The eluate was filtered, and the solvent was removed in vacuo.

2-tert-Butyl-4-[5-(2-tert-butylbenzopyran-4-ylidene)-1,3-pentadien-1-yl]benzopyrylium Perchlorate (IIIc). A mixture of 0.1 g (0.33 mmole) of salt IIa, 0.043 g (0.166 mmole) of (3-phenylamino-2-propenylidene)phenylammonium chloride in 1.5 ml of acetonitrile and 0.5 ml of acetic anhydride, and 0.039 g (0.5 mmole) of pyridine was refluxed for 3 min, after which the dye was removed by filtration and washed with acetic acid and ether.

2-[3-(4-tert-Butylbenzopyran-2-ylidene)-1-propen-1-yl]-4-tert-butylbenzopyrylium Perchlorate (IVa). A mixture of 0.1 g (0.33 mmole) of salt IIb and 0.47 g (3.2 mmole) of ethyl orthoformate in 1.5 ml of a mixture of acetonitrile with acetic anhydride (4:1) in the presence of 0.03 g (0.38 mmole) of pyridine was refluxed for 3 min, after which the dye was precipitated with 10% perchloric acid.

2-[3-(4-tert-Butylbenzopyran-2-ylidene)-1-propen-1-yl]-4-tert-butylbenzopyrylium Perchlorate (IVc). This compound was obtained in the same way as IVa starting from salt IIc.

2-[5-(4-tert-Butylbenzopyran-2-ylidene)-1,3-pentadien-1-yl]-4-tert-butylbenzopyrylium and 2-[5-(4-tert-Butylbenzothiopyran-2-ylidene)-1,3-pentadien-1-yl]-4-tert-butylbenzothiopyrylium Perchlorates (IVb, d). These compounds were synthesized in the same way as IIIc starting from salts IIb, c.

1,3,3-Trimethyl-2-[3-(2-tert-butylbenzopyran-4-ylidene)-1-propen-1-yl]-3H-indoliumPerchlorate (Va). A mixture of 0.3 g (1 mmole) of salt IIa and 0.2 g (1 mmole) of 1,3,3-trimethyl-2-formylmethyleneindoline in 2 ml of acetic anhydride was heated at 100°C for 10 min, after which the mixture was cooled, and the dye was precipitated with 20% perchloric acid.

2-tert-Butyl-4-[2-(4-dimethylaminophenyl)ethenyl]benzopyrylium Perchlorate (Vb). A mixture of 0.15 g (0.5 mmole) of salt IIa and 0.15 g (1 mmole) of p-dimethylaminobenzaldehyde in 1 ml of acetic anhydride was heated at 120°C for 30 min, after which the dye was removed by filtration and washed with ether.

1,3,3-Trimethyl-2-[3-(4-tert-butylbenzopyran-2-ylidene)-1-propen-1-yl]-3H-indolium and 1,3,3-Trimethyl-2-[3-(4-tert-butylbenzothiopyran-2-ylidene)-1-propen-1-yl]-3H-indoliumPerchlorates (VIa, c). These compounds were synthesized in the same way as Va using salts IIb, c.

2-[2-(4-Dimethylaminophenyl)ethenyl]-4-tert-butylbenzopyrylium and 2-[2-(4-Dimethylaminophenyl)ethenyl]-4-tert-butylbenzothiopyrylium Perchlorates (VIb, d). These compounds were obtained in the same way as Vb starting from salts IIb, c.

2-[3-(Benzopyran-2-ylidene)-1-propen-1-yl]benzopyrylium Perchlorate (VII). A mixture of 0.7 g (2 mmole) of 2-methylbenzopyrylium tetrachloroferrate [7] and 0.35 g (3 mmole) of ethyl orthoformate in 10 ml of absolute ethanol was refluxed for 10 min, after which the dye was removed by filtration, washed successively on the filter with ethanol and ether until the crimson color disappeared, dissolved in acetonitrile, and precipitated with saturated aqueous sodium perchlorate solution.

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