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PYROLOCYANINES.

17.* SYMMETRICAL FLAVYLOCYANINES BASED ON METHOXY-SUBSTITUTED 4-METHYLFLAVYLIUM SALTS

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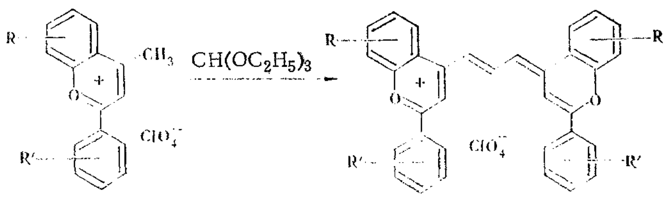
UDC 547.814.5.07:541.651:668.819.45:543.422

Symmetrical flavylocyanines in which electron-donor substituents (methoxy groups) are present alternately in the 5, 6, 7, 8, 2', 3', and 4' positions of the flavylium rings were synthesized. The characteristics of the long-wave absorption bands of the resulting flavylocyanines are discussed with the aid of quantum-chemical methods. It is shown that not only the position but also the form of their absorption bands can be changed purposefully by introduction of substituents in the heteroresidues of symmetrical polymethine dyes.

In the pyrylocyanine series the effect of annelation of benzene rings to the heteroresidues, as well as the effect of replacement of the oxygen atoms in the latter by sulfur or selenium atoms, on the spectral properties has been studied systematically [2]. Within the framework of our systematic investigation of this group of dyes it seemed of interest to also study the effect of substituents on their color. This problem was also worthy of consideration because of the fact that pyrylocyanines have recently found application in the technology of silverless light-sensitive materials [3] and quantum electronics [4], in which compounds that absorb over strictly predesignated wavelength ranges are required. In the present paper we describe symmetrical flavylocarbocyanines that contain methoxy groups in various positions of the flavylium residues. We selected trimethylidynecyanines as the subjects of the investigation, since, in contrast to monomethlidynecyanines, their molecules do not display effects due to close orientation of the rings [5], and solvation effects are not manifested as markedly as in the case of dyes with longer chromophores [6]. This should make it possible to follow more distinctly the influence of the electronic effects of substituents on the color.



Ia-h

II, III a-g

a $R=5\text{-}OCH_3$; b $R=6\text{-}OCH_3$; c $R=7\text{-}OCH_3$; d $R=8\text{-}OCH_3$; e $R'=2'\text{-}OCH_3$; f $R'=3'\text{-}OCH_3$; g $R'=4'\text{-}OCH_3$; h $R'=2'\text{-}OH$; II $R=R'=H$. Where not indicated, R or R' = H.

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*See [1] for communication 16.

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Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 304-308, March, 1983. Original article submitted June 8, 1982.

0009-3122/83/1903-0243$07.50

TABLE 1. Characteristics of the Long-Wave Absorption Bands of Solutions of Dyes II and IIa-g

Compound	R or R′	Solvent*	λ_{max}, nm	lg ε	M^{-1}, nm	f	σ, cm^{-1}	γ_1	γ_2	F	M^{-1}_{th}, nm	δ
II	H	1 [5]	715	5,31	695,9	0,83	772	1,60	3,4	0,110	698	0,1132
		2	704	5,28	680,6	0,99	863	1,56	3,1	0,105		
III a	5-OCH_3	1	706	5,31	685,9	1,02	867	1,57	3,2	0,107	682	0,1143
		2	696	5,20	668,1	0,92	969	1,53	3,0	0,107		
III b	6-OCH_3	1	728	5,37	709,5	0,92	715	1,65	3,8	0,117	707	0,1098
		2	718	5,13	693,2	0,79	802	1,58	3,2	0,107		
III c	7-OCH_3	1	702	5,40	686,9	1,30	776	1,59	3,3	0,108	688	0,1135
		2	696	5,30	671,5	1,01	861	1,58	3,5	0,114		
III d	8-OCH_3	1	712	5,34	691,8	0,99	750	1,62	3,5	0,113	695	0,1117
		2	702	5,22	678,6	0,85	836	1,51	3,0	0,107		
III e	2′-OCH_3	1	720	5,23	700,4	0,91	815	1,52	3,6	0,085	694	0,1099
		2	710	5,14	684,7	0,90	896	1,35	2,9	0,070		
III f	3′-OCH_3	1	716	5,30	697,1	0,92	778	1,58	3,6	0,105	698	0,1131
		2	706	5,11	681,6	0,83	871	1,57	3,6	0,104		
III g	4′-OCH_3	1	736	5,30	715,2	0,93	790	1,66	4,0	0,111	694	0,1093
		2	724	5,18	698,2	0,85	897	1,62	3,9	0,107		

*Methylene chloride is indicated by 1, and acetonitrile is indicated by 2.

We used isomeric 5-, 6-, 7-, 8-, 2'-, 3'-, and 4'-methoxy-substituted 4-methylflavylium salts (Ia-g) in the synthesis of the dyes. All of these salts, except the 7-substituted derivative, were obtained by condensation of substituted o-hydroxyacetophenones with acetophenone or o-hydroxyacetophenone with substituted acetophenones by a method similar to that described for 4-methyl-4'-methoxyflavylium perchlorate [7]. Salt impurities, which might have been formed as a result of self-condensation of the first of the reaction components, were not detected by PMR spectroscopy in the above-indicated synthesis, although O-hydroxyacetophenone itself is converted to 4-methyl-2'-hydroxyflavylium perchlorate (Ih) when the second component is absent. 4-Methyl-7-methoxyflavylium perchlorate was obtained in the same way as the 7-hydroxy-substituted salt [8] by condensation of resorcinol monomethyl ether with benzoylacetone, which was carried out under conditions similar to those used in the condensation of the same phenol with dibenzoylmethane [9]. Flavylotrimethylidynecyanines IIIa-g were obtained by condensation of the corresponding salts with ethyl orthoformate.

The spectral characteristics of unsubstituted flavylocyanine II [5] and the synthesized methoxy-substituted dyes are compared in Table 1. Data are presented for solutions in the slightly polar methylene chloride and the strongly polar acetonitrile. In addition to the generally accepted characteristics of the long-wave absorption bands (λ_{max}, log ε, and oscillator forces f), the average positions of the absorption bands (M^{-1}) and the characteristics of the forms of the bands, viz., the widths (σ) and the coefficients of asymmetry (γ_1), excess (γ_2), and the fine structure (F), are presented, as in [5]. In addition to the experimental data, the results of quantum-chemical calculations by the simple Hückel MO method of the average positions of the bands (M^{-1}_{th}) and the quadratic changes in the bond orders during excitation (δ) [10] are presented in Table 1. The latter characteristic, inasmuch as it is a quantitative measure of the vibron interactions, was responsible, in the absence of strong solvation effects, for the change in the width of the absorption band. It follows from the experimental M^{-1} values presented in Table 1 that the introduction of a methoxy group in the 6, 2', 3', and 4' positions of the heterocyclic residues of the dyes leads to deepening of the color, whereas introduction in the 5, 7, and 8 positions leads to heightening of the color, and this makes it possible to arrange the examined dyes in the following order with respect to heightening of the color:

$$4' > 6 > 2' > 3' \geq \text{without a substituent} > 8 > 7 > 5.$$

It is also apparent from Table 1 that a methoxy group in the 5, 2', and 4' positions gives rise to broadening of the absorption band, whereas a methoxy group in the 6 and 8 positions leads to contraction. The examined substituent in the 7 and 3' positions causes virtually no change in the width of the absorption band. The noted principles are valid both for solutions in the slightly polar methylene chloride and for solutions in the strongly polar acetonitrile, except that in the latter case the bands are broader, more asymmetrical, and more diffuse (as indicated by the smaller γ_1, γ_2, and F values) and are shifted to the shorter-wave region. It is significant that changes not only in the position of the absorption bands but also in their width under the influence of a substituent for each of the dyes obtained are almost independent of the solvent. For example, in the case of solutions in CH_2Cl_2 a methoxy group in the 6,6 positions of the dye gives rise to a 13.6 nm bathochromic shift of M^{-1} and a 57 cm^{-1} contraction of the absorption band, as compared with 12.6 nm and 61 cm^{-1} changes, respectively, in these characteristics in the same directions in the case of solutions in CH_3CN. This means that the examined substituents introduce virtually no changes in the solvation of the dye molecule but do affect its spectral characteristics by means of their electronic effect. The experimental data obtained are in good agreement with the quantum-chemical evaluation of the effect of an electron-donor substituent on the position and width of the absorption bands of flavylotrimethylidynecyanines (see M_{th}^{-1} and δ). In these calculations, which were made by means of the simple Hückel method, the effect of the methoxy group was modeled by means of the negative value of the coulombic integral (—0.2) of the carbon atoms of the flavylium ring to which this group was attached (the resonance integrals of the $C—OCH_3$ bond were assumed to be equal to zero, and $\beta_{CC} = \beta = -26400\ cm^{-1}$). The same values of the quantum-chemical parameters as those used in the calculation of unsubstituted flavylocarbocyanine [10] were used for the remaining atoms and bonds. Dyes IIIe and IIIg, which contain a substituent in the 2' and 4' positions and for which a long-wave shift of the absorption bands and a certain amount of broadening of these bands are observed, whereas the theoretical calculation predicts just the opposite changes in the indicated spectral characteristics, constitute an exception. This can be explained by a decrease in the torsion angle and, consequently, an increase in the order of the bond between the phenyl substituent and the heteroresidue due to the effect of conjugation of the latter with the methoxy group. In fact, a gradual increase in the resonance angle of the $C_{(2)}—C_{(1')}$ bond leads to an increase in M_{th}^{-1} (deepening of the color) and δ (broadening of the band). Thus if it is assumed that $\beta_{C_{(1')}—C_{(2)}} = 0.9\beta$ in the calculation of the 2'-methoxyflavylocyanine (IIIe) molecule instead of $\beta_{C_{(1')}—C_{(2)}} = 0.8\beta$, as has been assumed for a whole series of dyes, M_{th}^{-1} turns out to be equal to 707 nm, and $\delta = 0.1121$. When $\beta_{C_{(1')}-C_{(2)}} = 1.0\beta$ for the same molecule, it was found that $M_{th}^{-1} = 721$ nm and $\delta = 0.1145$. Similarly, $M_{th}^{-1} = 707$ nm and $\delta = 0.1114$ for dye III when $\beta_{C_{(1')}-C_{(2)}} = 0.9\beta$, whereas $M_{th}^{-1} = 727$ nm and $\delta = 0.1135$ when $\beta_{C_{(1')}-C_{(2)}} = 1.0\beta$.

Thus in the case of the examined flavylocyanines it was shown that one can purposefully regulate not only the position but also the form of the absorption bands by introduction of substituents in the heteroresidues of symmetrical polymethine dyes.

EXPERIMENTAL

The moments of the absorption bands were determined as in [10] on the basis of the absorption spectra of the dyes recorded at 200 cm^{-1} intervals with an SF-4A spectrometer with methylene chloride (stabilized with 1% C_2H_5OH) and acetonitrile as the solvents at layer thicknesses of 1 and 5 cm. The absorption spectra of solutions of the dyes were measured with an error of no less than two orders of magnitude in intensity. The numerical values in Table 1 are presented with an accuracy corresponding to the degree of the error in the measurement of the absorption spectra of the dyes. The UV spectra of the flavylium salts obtained were determined with the same apparatus with acetonitrile as the solvent. The PMR spectra of solutions of the compounds in CF_3COOH were determined with a Tesla BS-487-B spectrometer (60 MHz) at 20°C with hexamethyldisiloxane as the internal standard. The IR spectra of KBr pellets were recorded with a UR-20 spectrometer. The purity of the preparations was monitored by thin-layer chromatography (TLC) on Silufol UV-254 plates by elution with nitromethane.

4-Methyl-5-methoxyflavylium Perchlorate (Ia, Table 2). A mixture of 7.47 g (45 mmole) of 2-hydroxy-6-methoxyacetophenone [11], 5.26 ml (45 mmole) of acetophenone, and 6.33 ml (70 mmole) of 70% $HClO_4$ in 30 ml of glacial acetic acid was heated at 110°C for 3 h, after which it was cooled and treated with ether (80-100 ml), and the precipitate was removed by filtration and washed with ether. UV spectrum, λ_{max} (log ε): 419 nm (4.44). PMR spectrum: 3.76 (3H, s, OCH_3) and 2.68 ppm (3H, s, CH_3).

4-Methyl-6-methoxyflavylium Perchlorate (Ib). Compound Ia was similarly obtained from 2-hydroxy-5-methoxyacetophenone [12] by heating at 125°C for 4.5 h. UV spectrum, λ_{max} (log ε): 369 (4.34), 413 nm (4.22). PMR spectrum: 3.65 (3H, s, OCH_3) and 2.80 ppm (3H, s, CH_3).

4-Methyl-7-methoxyflavylium Perchlorate (Ic). Dry HCl was passed into a solution of 21 g (170 ml) of resorcinol monomethyl ether and 24 g (150 mmole) of benzoylacetone in 80 ml of

TABLE 2. Characteristics of the Synthesized Compounds

Compound	mp,* °C	Calc., %			Empirical formula	Yield, %			Yield, %
		C	H	Cl		C	H	Cl	
Ia	217—218	58,1	4,3	10,0	$C_{17}H_{15}ClO_6$	58,2	4,3	10,1	10
Ib	245—246	58,6	4,2	9,8	$C_{17}H_{15}ClO_6$	58,2	4,3	10,1	40
Ic	242 -243	58,2	3,9	10,2	$C_{17}H_{15}ClO_6$	58,2	4,3	10,1	70
Id	210—211	57,9	4,0	10,1	$C_{17}H_{15}ClO_6$	58,2	4,3	10,1	50
Ie	222—223	58,1	4,3	9,9	$C_{17}H_{15}ClO_6$	58,2	4,3	10,1	25
If	207--208	58,3	4,4	10,3	$C_{17}H_{15}ClO_6$	58,2	4,3	10,1	20
Ih	230—231	57,6	3,9	10,4	$C_{16}H_{13}ClO_6$	57,1	3,9	10,5	25
IIIa	298--299	68,7	4,7	5,7	$C_{35}H_{27}ClO_8$	68,8	4,4	5,8	40
IIIb	336	68,5	4,3	6,0	$C_{35}H_{27}ClO_8$	68,8	4,4	5,8	22
IIIc	342	68,6	4,4	6,0	$C_{35}H_{27}ClO_8$	68,8	4,4	5,8	89
IIId	323	68,5	4,5	5,7	$C_{35}H_{27}ClO_8$	68,8	4,4	5,8	27
IIIe	278	69,1	4,4	5,6	$C_{35}H_{27}ClO_8$	68,8	4,4	5,8	33
IIIf	292	68,7	4,4	5,4	$C_{35}H_{27}ClO_8$	68,8	4,4	5,8	33
IIIg	308	68,7	4,5	5,6	$C_{35}H_{27}ClO_8$	68,8	4,4	5,8	70

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*The following solvents were used for crystallization: acetic acid for Ia,d-h, acetonitrile for Ib and IIIa,c,d, acetic acid—acetic anhydride (1:1) for IIIe-g, acetic acid—formic acid (3:2) for Ic, and CH_3COOH—$HCOOH$ (1:1) for IIIb.

glacial acetic acid for 2.5 h while maintaining the temperature at no higher than 20°C, after which the salt was precipitated with excess 42% $HClO_4$. The precipitate was removed by filtration and washed with acetic acid, benzene, and ether. UV spectrum, λ_{max} (log ε): 418 nm (4.58). PMR spectrum: 3.75 (3H, s, OCH_3) and 2.68 ppm (3H, s CH_3).

4-Methyl-8-methoxyflavylium Perchlorate (Id). This compound was obtained from 2-hydroxy-3-methoxyacetophenone [13] by a method similar to that used to obtain Ib by heating for 2 h. UV spectrum, λ_{max} (log ε): 381 nm (4.39). PMR spectrum: 3.80 (3H, s, OCH_3) and 2.75 ppm (3H, s, CH_3).

2'-Methoxy-4-methylflavylium Perchlorate (Ie). A mixture of 5.0 g (37 mmole) of o-hydroxyacetophenone, 5.6 g (37 mmole) of o-methoxyacetophenone [14], and 5.2 ml (60 mmole) of 70% $HClO_4$ in 20 ml of glacial acetic acid was heated and worked up as in the preparation of Ib. UV spectrum, λ_{max} (log ε): 3.59 (4.12) and 425 nm (4.32). PMR spectrum: 3.73 (3H, s, OCH_3) and 2.72 ppm (3H, s, CH_3).

3'-Methoxy-4-methylflavylium Perchlorate (If). This compound was obtained from m-methoxyacetophenone [14] by heating for 2 h as in the preparation of Ie. UV spectrum, λ_{max} (log ε): 374 nm (4.39). PMR spectrum: 3.61 (3H, s, OCH_3) and 2.78 ppm (3H, s, CH_3).

2'-Hydroxy-4-methylflavylium Perchlorate (Ih). A mixture of 13.6 g (100 mmole) of o-hydroxyacetophenone and 14.0 ml (150 mmole) of 70% $HClO_4$ in 75 ml of glacial acetic acid was heated and worked up as in the preparation of Ib. UV spectrum, λ_{max} (log ε): 362 (4.17) and 424 nm (4.39). PMR spectrum: 2.70 ppm (3H, s, CH_3). IR spectrum: 3200-3300 cm^{-1} (O—H).

4-[3-(5-Methoxy-4-flavenylidene)-1-propenyl]-5-methoxyflavylium Perchlorate (IIIa). A mixture of 0.210 g (0.6 mmole) of salt Ia, 0.050 g (0.6 mmole) of anhydrous CH_3COONa, and 0.164 g (1.8 mmole) of freshly distilled ethyl orthoformate in 2.5 ml of distilled acetic anhydride was refluxed vigorously for 10 min, after which it was cooled, and the precipitate was removed by filtration and washed with a small amount of acetic anhydride, acetic acid, water, acetic acid, benzene, and ether.

4-[3-(6-Methoxy-4-flavenylidene)-1-propenyl]-6-methoxyflavylium perchlorate (IIIb), 4-[3-(7-methoxy-4-flavenylidene)-1-propenyl]-7-methoxyflavylium perchlorate (IIIc), 4-[3-(8-methoxy-4-flavenylidene)-1-propenyl]-8-methoxyflavylium perchlorate (IIId), 4-[3-(2'-methoxy-4-flavenylidene)-1-propenyl]-2'-methoxyflavylium perchlorate (IIIe), 4-[3-(3'-methoxy-4-flavenylidene)-1-propenyl]-3'-methoxyflavylium perchlorate (IIIf), and 4-[3-(4'-methoxy-4-flavenylidene)-1-propenyl]-4'-methoxyflavylium perchlorate (IIIg) were obtained in the same way as IIIa from salts Ib-f and 4'-methoxy-4-methylflavylium perchlorate [7], respectively (Table 2).

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SYNTHESIS OF (4aR,9aS,9bR)- AND (4aR,9aS,9bS)-4a,6,6,9a-TETRAMETHYL-trans-PERHYDROINDANO[2,1-c]PYRANS

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UDC 547.659.1'665'728.2'816:542.953.2:543.422.51

$C_{(9b)}$-Epimeric (4aR,9aS)-4a,6,6,9a-tetramethyl-trans-perhydroindano[2,1-c]pyrans, which have the odor of ambergris, were synthesized by dehydration of the corresponding glycols. It was established that a mixture of epimeric [with respect to $C_{(3a)}$] (8aS,8bR)-5,5,8a-trimethyl-3a-ethyl-trans-perhydroindano[2,1-b]furans is formed along with a trans-perhydroindano[2,1-c]pyran derivative in the acidic dehydration of (1R,2R,7aS)-2,4,4,7a-tetramethyl-1-(2-hydroxyethyl)-2-hydroxymethyl-trans-hydrindan.

It is known [1, 2] that a number of products of the cleavage of labdane diterpenoids with the composition C_{16}-C_{18} have the odor of ambergris and are of interest to the perfume industry as substitutes for the scarce and costly ambergris derived from whales.

According to the existing concepts [2-4], the odor of ambergris is peculiar to trans-decalin derivatives that contain the I structural fragment with three axial substituents in the 2, 4a, and 8a positions and an oxygen-containing functional group attached to one of these centers (Ohloff's 1,2,4-triaxial rule).

In order to verify this rule it seemed of interest to synthesize substances with structures similar to those of the indicated decalin compounds, which, however, do not satisfy its requirements. In our opinion, derivatives of trans-perhydronaphtho[2,1-c]pyran and trans-perhydroindano[2,1-c]pyran are compounds of this sort.

In the present communication we describe the synthesis of (4aR,9aS,9bR)- and (4aR,9aS,-9bS)-4a,6,6,9a-tetramethyl-trans-perhydroindano[2,1-c]pyrans (II and III).

Compound II was synthesized on the basis of (1R,8aS)-Δ^2-1-(2-hydroxyethyl)-2,5,5,8a-tetramethyl-trans-octahydronaphthalene (IV) [5] (see Scheme 1). Acetylation of alcohol IV

Institute of Chemistry, Academy of Sciences of the Moldavian SSR, Kishinev 277028. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 309-314, March, 1983. Original article submitted April 26, 1982.

0009-3122/83/1903-0247$07.50