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PYRYLOCYANINES.

23.* 2-PYRYLOCARBOCYANINES WITH SUBSTITUENTS IN HETERO RESIDUES

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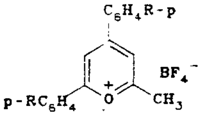
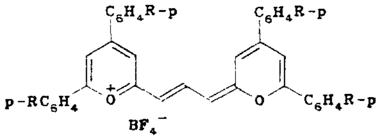
Symmetric 2-pyrylo- and asymmetric (indo)(2-pyrylo)trimethinecyanines with substituents of different electronic nature in the pyran residue were synthesized. The influence of the conjugation effect and inductive effect on the characteristics of absorption bands of the synthesized dyes was analyzed by a quantum chemical calculation according to a common MO Hückel method.

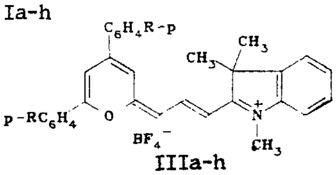
In [2, 3] we studied the influence of an electron-donor methoxy group on the position and form of absorption bands of symmetric and asymmetric 2-pyrylocarbocyanines. However, similar studies for other substituents in this class of dyes are not available. These investigations are required to establish the general relationship between the electronic effect of the substituents and the spectral properties of pyrylocyanines. To solve this problem, we synthesized symmetric (IIa-h) and asymmetric (IIIa-h) α-pyrylocarbocyanines.



Ia-h



IIa-h



IIIa-h

I—III a R=H, b R=OCH_3, c R=OC_2H_5, d R=CH_3, e R=F, f R=Cl, g R=Br, h R=NO_2

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*For Communication 22, see [1].

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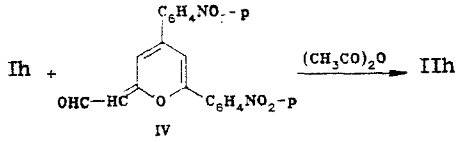
TABLE 1. Characteritics of Long-Wave Absorption Bands of Dyes IIa-h and IIIa-h in CH_2Cl_2

Dye	λ_{max}, nm	log ε	M^{-1}, nm	D_M, nm	f	σ, cm^{-1}	γ_1	γ_2	F
IIa	730, 800	4,77; 4,93	739,6		0,78	1176	1,17	2,2	0,064
IIb	746, 824	4,70; 4,92	769,5		0,80	1079	1,20	2,0	0,079
IIc	750, 830	4,71; 4,93	769,9		0,81	1072	1,20	2,1	0,081
IId	730, 810	4,77; 4,95	749,8		0,84	1126	1,18	2,3	0,079
IIe	730, 800	4,77; 4,92	741,6		0,79	1150	1,18	2,3	0,070
IIf	740, 815	4,75; 4,88	755,5		0,72	1270	1,13	1,8	0,059
IIg	745, 820	4,75; 4,88	757,9		0,71	1220	1,14	2,0	0,060
IIh	760, 830	4,62; 4,59	759,7		0,60	1370	1,08	1,5	0,054
IIIa	654, 682	4,71; 4,63	641,1	−8,3	0,76	1450	0,89	1,5	0,031
IIIb	664, 700	4,78; 4,79	654,9	−7,2	0,81	1324	1,26	3,0	0,054
IIIc	664, 700	4,78; 4,81	655,3	−7,4	0,83	1303	1,30	3,3	0,058
IIId	665, 700	4,76; 4,71	651,9	−14,0	0,79	1375	1,15	2,1	0,040
IIIe	658, 700	4,75; 4,64	644,0	−10,2	0,77	1397	1,14	1,9	0,038
IIIf	665, 700	4,74; 4,61	646,0	−5,3	0,68	1680	0,92	1,3	0,028
IIIg	670, 710	4,75; 4,62	649,1	−7,2	0,66	1570	1,03	1,5	0,030
IIIh	645, 690	4,58; 4,54	635,2	7,7	0,56	2160	0,87	1,1	0,025

For their preparation, we used tetrafluoroborates of 2-methyl-4,6-diarylpyrylium salts (Ia-h), synthesized by the method in [4]. The previously unknown fluorine-substituted salt Ie was obtained by condensing p-fluoroacetophenone with acetic anhydride in the presence of boron trifluoride etherate. The synthesis of the symmetric dyes IIa-h has several characteristic features related to the influence of the nature of the substituent. Pyrylocyanine IIa was synthesized by condensing the initial pyrylium salt Ia with ethyl orthoformate in a mixture of acetic acid and acetic anhydride in the presence of sodium acetate [5]. Dyes IIa-g were obtained by heating the corresponding salts Ib-g with ethyl orthoformate in acetic anhydride, using pyridine as the condensing agent. The nitro-substituted trimethinecyanine IIh could not be obtained chromatographically pure by condensing salt Ih with the orthoformic ester, but it was synthesized in this state of purity from 4,6-di-(p-nitrophenyl)-formylmethylene-2H-pyran (IV) according to the scheme:



The asymmetric dyes IIIa-h were obtained by the reaction between pyrylium salts Ia-h and 1,3,3-trimethyl-2-formylindoline in acetic anhydride.

Besides λ_{max} and log ε, in Table 1, as well as in [2, 3], data are given for solutions of the dyes in methylene chloride on the mean positions of the absorption bands M^{-1}, determined by the method of moments, the oscillator forces f, and the characteristics of band forms (widths σ, asymmetry coefficients γ_1, excess γ_2, and fine structure F).

Analysis of the data in Table 1 reveals an unusual redistribution of absorption intensities: In particular the vibrational maximum, depending on the nature of the substituent, may have an absorption intensity both lower or higher than that of the principal maximum, not only for asymmetric, but also for symmetric dyes. Therefore, in a discussion of the regularities in the color of pyrylocyanines IIa-h and IIIa-h, we shall use the values of M^{-1} and not λ_{max}.

In symmetric dyes, all the substituents, regardless of the electronic nature, cause deepening of the color. In asymmetric pyrylocyanines, the introduction of a nitro group, a typical electron-acceptor, leads to a hypsochromic shift of M^{-1}. All the remaining substituents, as in symmetric dyes, cause a bathochromic shift of the mean positions of the bands (Table 1).

According to their influence on the form of the bands of both symmetric and asymmetric dyes, the substituents can be divided into two groups: OCH_3, OC_2H_5, CH_3, and F cause narrowing of the absorption bands, increasing their intensity, asymmetry, excess, and structurization, while Br and Cl atoms and the NO_2 group cause opposite changes in the spectra. This course of σ and γ_1, γ_2, and F indicates that changes in band widths are mainly determined by the vibronic interactions (V.I.). Their degree can be quantitatively characterized by the value of quadratic changes in the bond orders δ [6].

TABLE 2. Results of Quantum Chemical Calculations

Compound	α_R	β_{C-R}	$\alpha_{C_{(4)}}$	$\beta_{C-C_6H_5}$	M^{-1}_{theor}	δ	Φ_0
IIa	—	—	—	0,8	740	0,1723	37,6
IIb, c	2	0,8	0,2	1	798	0,1645	38,4
IId	2	0,7	0,2	0,8	744	0,1708	38,1
	(2)	(0,7)	(0)	(0,8)	(734)	(0,1649)	(40.2)
	(2)	(0)	(0,2)	(0,8)	(751)	(0,1779)	(35,4)
IIe	2,5	0,85	0,25	0,8	743	0,1710	38,0
	(2,5)	(0,85)	(0)	(0,8)	(732)	(0,1637)	(40,7)
	(2,5)	(0)	(0,25)	(0,8)	(754)	(0,1793)	(34,8)
IIf	2	0,4	0,2	0,8	748	0,1757	36,3
	(2)	(0,4)	(0)	(0,8)	(738)	(0,1669)	(38,5)
IIg	1,5	0,3	0,15	0,8	746	(0,1748)	(36,6)
	(1,5)	(0,3)	(0)	(0,8)	(739)	(0,1705)	(38,3)
	(1,5)	(0)	(0,15)	(0,8)	(748)	(0,1766)	(36,0)
IIh	1,5	1	0,15	0,8	765	0,1807	34,0
	(1,5)	(1)	(0)	(0,8)	(756)	(0,1766)	(35,7)

We should note that the spectral characteristics of compounds IIa, b, IIIa, b, and those of analogous dyes with a perchlorate anion [2, 3] are identical. Hence, the differences in the spectra of substituted pyrylocyanines are not due to ionic pairs [7]. They should be determined mainly by the electronic effect of the substituents, since the latter do not change the structural type of the dye or its conformation. To analyze this effect, we carried out quantum-chemical calculations by a common MO Hückel method of the values of the mean positions of the bands (M_{theor}^{-1}) and the values of δ (Table 2). In the calculation the influence of the substituents is described by a hetero atom model [8], in which the donor properties of the substituent are determined by the ability of its unshared pair to participate in the conjugation (the conjugation effect). This ability is determined by the value of resonance β- and Coulombic α-integrals of the C—R bond and the substituent R, respectively. The electron-acceptor properties of the substituent, determined by its inductive effect, were modeled by a change at the α-carbon atom at the 4'-position, i.e., by the introduction of an auxiliary inductive parameter [8]. It was assumed to be equal to $0.1\alpha_R$ in all cases. The values of α_R and β_{C-R} for —OAlk, CH_3, Br, and Cl were taken from [8], and for the remaining atoms and bonds from [1]. The values of $\beta = -28{,}235\ cm^{-1}$. The parameters for the NO_2 group and F atom, available in the literature, were selected from data on the reactivity of the compounds and, therefore, were unsatisfactory for calculating the spectral characteristics of the dyes. For pyrylocarbocyanine IIg, $M_{theor}^{-1} = 5180$ nm. The value obtained is too high, because, at these parameters, the vacant level of the NO_2 group lies so low that the first electronic transition is localized on this group. It is localized in the main chromophore when α_N is decreased, which leads to increase in the NO_2 group levels, and also when β_{NO_2} is increased, which intensifies the repulsion of the levels. Satisfactory values of M_{theor}^{-1} for dye IIh were obtained at $\alpha_N = 1.5$, $\beta_{NO} = 2$, $\alpha_0 = \alpha_C + \beta$ [8]. For the fluorine containing pyrylocyanine IIe, the $_F$ had also to be decreased and β_{C-F} increased since the calculation with the latter assumes a strong influence of the F atom on its spectral characteristics (for IIe with parameters [8] $M_{theor}^{-1} = 757$ nm, $\delta = 0.1807$). This contradicts the experimental results and the data in review [9], which show that the introduction of an F atom into the hetero-residues of the dyes has practically no influence on color.

Table 2 shows (data in parentheses) that when the substituents exhibit only electron-donor properties ($\alpha_{C_{(4)}}' = 0$), we should expect an increase in color and decrease in the quadratic changes in the bond orders when R is introduced at the 4' position of an unsubstituted pyrylocarbocyanine IIa. Substituents with a pure electron-acceptor effect ($\beta_{C-R} = 0$) should cause opposite changes in the spectra (Table 2, data in parentheses). In an actual case, the predominance of one of these effects over the other will determine the regularities in the color of the substituted dyes.

A comparison of M_{theor}^{-1} of methyl- and chloro-substituted compounds with equal α_R, but different β_{C-R} (Table 2), shows that the bathochromic shift of the absorption band on transition from dye IId to IIf is due to weakening of the electron-donor properties of the Cl atom, compared with the methyl group, due to decrease in the conjugation effect ($\beta_{C-Cl} < \beta_{C-CH_3}$). However, despite the fact that $\beta_{C-O} > \beta_{C-CH_3}$ ($\alpha_{CH_3} = \alpha_{OAlk}$), the alkoxy-substituted pyrylocyanines IIb, c are more intensely colored than the methyl-substituted dye IId. This is explained by the fact that the introduction of OCH_3 and OC_2H_5 groups into the phenyl ring intensifies their conjugation not only with this ring, but also the conjugation of phenyl with the principal chromophore of the dyes, as follows from [2, 10]. We took this fact into account in the quantum chemical calculation, assuming, as in [2, 10] that for compound IIb, c, $\beta C\text{-}C_6H_5 = 1$ (in the remaining compounds, $\beta C\text{-}C_6H_5 = 0.8$). In fact, with such a supposition, they have the most intense color among the compounds studied. We should note that the model of the hetero atom used in this work for the alkoxy group gives the same tendencies in the change in M_{theor}^{-1} and δ as the model in [2, 10], in which this group was described by a negative Coulombic integral of the carbon atom bound to it.

The nitro group has the strongest electron-acceptor properties of all the substituents studied. This is evident not only from the inductive effect but also from the conjugation effect (see Table 2 at $\alpha C_{(4)}' = 0$). Therefore, as expected from the calculation, pyrylocyanine IIh is most intensely colored among the dyes with the same $\beta C\text{-}C_6H_5$ (Tables 1 and 2).

Considerable complications arise when substituents not only with different $\beta C\text{-}R$ but also with different αR are compared. Thus, when Cl atoms are substituted by Br atoms, decrease in $\beta C\text{-}R$ weakens the electron-donor properties of the substituent, but also increases them due to decrease in αR. Calculation assumes an increase in color on transition from dye IIf to IIg, i.e., increase in the electron-donor properties of the substituent (weakening of the electron-acceptor properties). The experimental data indicate that M^{-1} of pyrylocyanine IIg is, in contrast, bathochromically shifted with respect to IIf. This contradiction is due to the fact that the regularities in the color of halogen-substituted dyes are determined not only by an electronic effect of the substituent, but also by its polarizability [11], which is not accounted for in the quantum-chemical calculations. Comparison of the M_{theor}^{-1} values of compounds IIe, f shows that the electronic effects of the Cl and Br atoms differ little, while the polarizability of the latter compound is considerably higher than that of the former, which probably causes a bathochromic shift of the band on transition from a Cl- to a Br-substituted dye.

It is difficult to come to an unequivocal conclusion on the electronic influence of the halogens as well as other substituents with different $\beta C\text{-}R$ and αR on the color of the dyes studied, also because the changes may be due to the elongation of the chromophore in the direction of R. This may explain, as in [12], the fact that, regardless of their electronic nature, all the substituents studied cause a bathochromic shift of the bands in symmetric pyrylocyanines, compared with the unsubstituted dye IIa. A stricter criterion used to clarify this should be the width of the bands, since for the compounds studied the width is a function of vibronic interactions (V.I.), and their degree is determined by the value of alternation of the orders of all the conjugated bonds, irrespective of the directivity of the chromophore. The alternation value depends on the redistribution of the electron density on the chromophore atoms, which is mainly determined by a change in the electronic effect of the substituent, and not its polarizability. A narrowing of the band of the symmetric dye IIa when OCH_3, OC_2H_5, Ch_3 groups and F atom are introduced into its hetero residues (compounds IIb-e) shows the predominance of the conjugation effect over the inductive effect. Hence, the above substituents behave as electron-donors. In contrast, broadening of the band when hydrogen atoms at these positions are substituted by Cl, Br atoms or the NO_2 group (compounds IIf-h) indicates the predominating role of the electron-acceptor properties of these substituents (Tables 1 and 2) (predominance of the inductive effect over the conjugation effect).

In the spectra of asymmetric dyes IIIa-h, the effects should be mainly determined by a change in their electronic asymmetry, which in turn depends on the difference in the electron-donor capacities (basicities) of the hetero residues. It was impossible to come to any conclusion on the basicity of the terminal groups according to deviations D_M (they, in general, acquire negative values) which, as in [3], is probably due to a strong difference in the absorption areas of the parent dyes (>200 nm with respect to M^{-1}). From the results of the quantum-chemical calculations of theoretical electron-donor capacities Φ_0 [13]. The substituents can be arranged into the following series: $OC_2H_5(OCH_3) > CH_3 > F > H > Br > Cl > NO_2$ (Table 2). For the indolium ring, $\Phi_0 = 41°$ [13]. We should thus expect an increase in color and broadening of the bands in the same sequence, since decrease in the electron-donor capacity of the pyran residue when substituents are introduced into it, should intensify the electronic asymmetry (increase in the alternation of bonds). In fact, Tables 1 and 2 show that an increase in σ corresponds to a decrease in Φ_0. It is interesting to note that a similar correspondence is also observed in symmetric dyes IIa-h. This is explained

TABLE 3. Characteristics of Synthesized Dyes

Dye	mp,* °C	Found, %			Empirical formula	Calculated, %			Yield, %
		C	H	N (R)		C	H	N (R)	
IIa	140—141	74,9	4,6		$C_{37}H_{27}BF_4O_2$	75,3	4,6		63
IIb	242—243	63,0	5,0	(OCH_3 17,1)	$C_{41}H_{35}BF_4O_6$	63,3	5,0	(OCH_3 17,5)	53
IIc	160—161	70,1	5,8	(OC_2H_5 23,2)	$C_{45}H_{43}BF_4O_6$	70,5	5,7	(OC_2H_5 23,5)	57
IId	173—174	76,5	5,2		$C_{41}H_{35}BF_4O_2$	76,2	5,5		45
IIe	294—295	66,9	3,6	(F 22,6)	$C_{37}H_{23}BF_8O_2$	67,1	3,5	(F 23,0)	41
IIf	265—266	61,0	3,7	(Cl 19,2)	$C_{37}H_{23}BCl_4F_4O_2$	61,0	3,3	(Cl 19,5)	67
IIg	280—281	48,6	2,6	(Br 35,2)	$C_{37}H_{23}BBr_4F_4O_2$	49,0	2,6	(Br 35,3)	61
IIh	273—274	57,7	2,8	7,2	$C_{37}H_{23}BF_4N_4O_{10}$	57,7	3,0	7,3	51
IIIa	149—150	71,8	5,3	2,6	$C_{31}H_{28}BF_4NO$	72,0	5,5	2,7	82
IIIb	140—141	68,3	5,3	2,2	$C_{33}H_{32}BF_4NO_3$	68,4	5,6	2,4	71
IIIc	144—145	69,8	6,2	2,5	$C_{35}H_{36}BF_4NO_3$	69,4	6,0	2,3	74
IIId	252—253	72,7	6,3	2,6	$C_{33}H_{32}BF_4NO$	72,7	5,9	2,6	65
IIIe	221—222	67,6	4,9	(F 20,4)	$C_{31}H_{26}BF_6NO$	67,3	4,7	(F 20,6)	64
IIIf	251—252	64,0	5,0	2,4	$C_{31}H_{26}BCl_2F_4NO$	64,1	4,9	2,4	66
IIIg	279—280	54,9	4,4	2,0	$C_{31}H_{26}BBr_2F_4NO$	55,2	4,6	2,1	79
IIIh	260—261	61,3	4,3	6,8	$C_{31}H_{26}BF_4N_3O_5$	61,3	4,3	6,7	68

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*Compounds IIb-d, h are crystallized from nitromethane; IIe-g from a mixture of acetic acid with acetic anhydride (1:1); IIIa-g from acetic acid; IIIh from acetic anhydride.

by the fact that broadening of the absorption bands in the above series of substituents, in both asymmetric IIa-h and in symmetric pyrylocyanines IIIa-h, is due to increase in bonds alternation. The difference consists in that, in compounds IIa-h, it intensifies from ring to ring with increase in the difference in the electron-donor capacities of the terminal groups, and in compounds IIIa-h, from the center of the polymethine chain to the rings with increase in deviation of the hetero residues from the mean electron-donor capacity (Φ_0 = 45°), i.e., from the ideal polymethine state [13] (in this state all the bonds become straightened, and hence V.I. are minimal).

A comparison of Φ_0 and M^{-1} of compounds IIIa-g also confirms the above suppositions on the change in color of these dyes. At first glance, dyes IIIf, g are excluded from this regularity. They are more intensely colored than the unsubstituted dye IIIa. This can be explained by the fact that transition from IIIa to IIIf, g is accompanied by a weak change in the electron asymmetry, since the Φ_0 values of chloro- and bromo-substituted and unsubstituted residues are very similar, and the effective length [13] of the pyrylium residue increases fairly considerably when Cl and Br atoms are introduced into it. On transition from the symmetric pyrylocarbocyanine IIIa to IIf, g, M^{-1} undergoes a bathochromic shift (of 15.9 and 18.3 nm, respectively). Therefore, increase in the electronic asymmetry is insufficient to increase the color on transition from dye IIa to IIf, g, and only causes a decrease in the value of the bathochromic shift (in IIf by 4.9 nm and in IIg by 8 nm).

We can thus use as a guide the regularities found in the present work to predict changes in the position and width of the absorption band of pyrylocyanines, depending on the electronic nature of the substituents.

EXPERIMENTAL

The moments of the absorption bands were determined in a similar way as in [1-3] from the absorption spectra taken on an SF-4A spectrophotometer in CH_2Cl_2 with addition of 1% C_6H_5CN. The purity of the preparations was controlled by TLC on Silufol UV-254 plates, using acetonitrile as eluent. The characteristics of all the dyes synthesized are given in Table 3.

2-Methyl-4,6-di(p-fluorophenyl)pyrylium Tetrafluoroborate (Ie). A mixture of 27.6 g (0.2 mole) of p-fluoroacetophenone [14], 40.8 g (0.4 mole) of acetic anhydride, and 20.2 g (0.15 mole) of boron trifluoride etherate is boiled for 2 h. The hot reaction mixture is poured into 300 ml of ethyl acetate, and boiled for 5 min. The insoluble residue is filtered from the hot solution, washed on the filter by hot ethyl acetate (2 × 50 ml), and recrystallized from acetic acid to yield 11.8 g (32%) of Ie, mp 232-235°C, λ_{max} 350, 385 nm (CH_2Cl_2), ε_{max} $(2.1, 2.8)\cdot 10^4$. Found, %: C 58.8, H 3.8, F 30.9. $C_{18}H_{13}BF_6O$. Calculated, %: C 58.4, H 3.5, F 30.8.

2-[3-(4,6-Diphenyl-2-pyranylidene)-1-propenyl]-4,6-diphenylpyrylium tetrafluoroborate (IIa) is obtained from 0.167 g (0.5 mmole) of salt Ia, 0.150 g (0.1 mmole) of orthoformic ester, and 0.05 g of anhydrous sodium acetate by heating in 3 ml of a mixture of acetic anhydride and acetic acid (1:1) at 110-115°C for 30 min. The dye is filtered and washed with acetic acid and ether. The product is recrystallized from nitromethane.

Synthesis of Symmetric (2-Pyrylo)trimethinecyanines (IIb-g). A mixture of 0.5 mmole of the corresponding 2-methyl-4,6-diarylpyrylium tetrafluoroborate (IIb-g) and 0.150 g (1 mmole) of orthoformic ester in 2 ml of acetic anhydride with 4 drops of pyridine is boiled for 2 min. The dye is filtered and recrystallized.

2-[3-(4,6-Di-p-nitrophenyl-2-pyranylidene)-1-propenyl]-4,6-di(p-nitrophenyl)pyrylium Tetrafluoroborate (IIh). 4,6-Di(p-nitrophenyl)-2-formylmethylene-2H-pyran (IV) is synthesized in a similar way as its unsubstituted analog [15] by saponifying a monoiminium salt obtained from 0.424 h (0.1 mole) of salt Ih and 0.3 g (4 mmoles) of DMFA in 4 ml of acetic anhydride, by 40 ml of a 2% sodium hydroxide solution. Yield 50%. The compound is used further without purification. A mixture of 0.20 g (0.55 mmole) of derivative IV and 0.21 g (0.5 mmole) salt Ih in 2 ml of a mixture of acetic anhydride and acetic acid (1:1) is heated to boiling for 2 min, and 0.2 g of compound IIh is filtered.

Synthesis of Asymmetric (Indo)(2-pyrylo)trimethinecyanines (IIIa-h). A mixture of 1 mmole of the corresponding 2-methyl-4,6-diarylpyrylium tetrafluoroborate (Ia-h) and 0.25 g (1.2 mmole) of 1,3,3-trimethyl-2-formylmethyleneindoline is heated in 10 ml of a mixture of acetic anhydride and acetic acid (1:1) at boiling point for 5 min. The dye is filtered and recrystallized.

LITERATURE CITED

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