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PYRYLOCYANINES.

18.* UNSYMMETRICAL FLAVYLOCYANINES ON THE BASIS OF METHOXY-SUBSTITUTED 4-METHYLFLAVYLIUM SALTS

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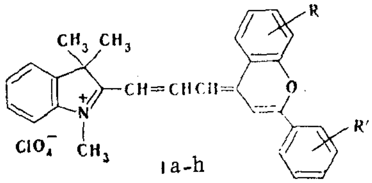
UDC 547.814.5'753:541.651:668.819.45

Unsymmetrical flavyloindotrimethylidynecyanines in which a methoxy group is located alternately in the 5, 6, 7, 8, 2', 3', and 4' positions of the flavylium ring were synthesized. An increase in the electron-donor character of the heterocyclic residue generally leads to a bathochromic shift of the absorption bands of the dyes and a decrease in the widths of these bands and the ratios of the intensities of the short-wave and long-wave maxima in them.

Previously in the case of a number of unsymmetrical polymethine dyes that differ with respect to the structure of one of the heterocyclic residues it was shown that the form of their long-wave absorption bands changes as the electronic asymmetry of the dye changes [2]. The indicated principle should be observed more distinctly in the case of unsymmetrical dyes with a monotypic structure, the electronic asymmetry of which changes only under the influence of the introduction of substituents into one of the heteroresidues. With this in mind, in the present research we synthesized a number of substituted derivatives of flavyloindotrimethylidynecyanine (Ia), which contain a methoxy group in various positions of the flavylium residue (Ib-h). Dyes Ib-h were obtained by condensation of the corresponding substituted 4-methylflavylium salts [1] with 1,3,3-trimethyl-2-formylmethyleneindoline in acetic anhydride.



Ia-h

b $R=5\text{-}OCH_3$; c $R=6\text{-}OCH_3$; d $R=7\text{-}OCH_3$; e $R=8\text{-}OCH_3$; f $R'=2'\text{-}OCH_3$; g $R'=3'\text{-}OCH_3$; h $R'=4'\text{-}OCH_3$ (unindicated R, $R'=H$)

The spectral characteristics of solutions of dyes Ia-h in methylene chloride and acetonitrile are compared in Table 1. In the case of long-wave absorption bands that have two maxima we present the positions of these maxima and their extinctions, as well as the average positions of the bands (M^{-1}) (obtained by the method of moments), their deviations (D_M), the oscillator forces (f), the widths (σ), and the coefficients of asymmetry (γ_1), excess (γ_2), and fine structure (F). When one compares the average positions of the absorption bands, it is apparent that in both the slightly polar methylene chloride and the strongly polar acetonitrile the dyes obtained (except for Ie) are more deeply colored than unsubstituted dye Ia. The introduction of a methoxy group in the 8 position (dye Ie) has virtu-

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*See [1] for communication 17.

Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev 252660. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1189-1191, September, 1983. Original article submitted June 16, 1982; revision submitted March 9, 1983.

0009-3122/83/1909-0948$07.50

TABLE 1. Characteristics of the Long-Wave Absorption Bands of Solutions of Dyes Ia-h

Compound	Solvent	λ_{max}, nm	M^{-1}, nm	D_M, nm	lg ε	$\varepsilon_1/\varepsilon_2$	f	σ, cm^{-1}	γ_1	γ_2	F
Ia	CH_2Cl_2 [4]	595, 640	586,8	24,2	4,69; 4,66	1,07	0,72	1593	1,09	2,8	0,053
	CH_3CN	582, 626	559,1	41,1	4,65; 4,52	1,37	0,80	1911	1,26	3,0	0,061
Ib	CH_2Cl_2	596, 636	588,5	17,5	4,84; 4,87	0,90	0,98	1524	1,43	3,6	0,074
	CH_3CN	584, 624	563,9	30,1	4,77; 4,68	1,22	1,18	1726	1,11	2,3	0,049
Ic	CH_2Cl_2	604, 646	600,9	16,9	4,86; 4,91	0,89	0,98	1327	1,09	1,9	0,051
	CH_3CN	592, 636	577,1	29,4	4,84; 4,77	1,16	1,05	1614	0,97	1,5	0,044
Id	CH_2Cl_2	598, 638	596,4	10,1	4,88; 4,95	0,84	1,01	1240	1,12	1,9	0,052
	CH_3CN	588, 630	575,6	20,1	4,83; 4,81	1,05	1,01	1578	1,21	2,5	0,058
Ie	CH_2Cl_2	598, 639	585,8	23,1	4,76; 4,76	0,98	0,87	1570	1,23	2,8	0,057
	CH_3CN	584, 626	558,6	40,6	4,64; 4,54	1,29	0,80	1878	1,18	2,6	0,057
If	CH_2Cl_2	602, 648	600,4	12,8	4,83; 4,88	0,87	0,93	1346	1,11	1,9	0,053
	CH_3CN	590, 634	572,2	30,1	4,78; 4,69	1,22	0,96	1614	1,01	1,7	0,044
Ig	CH_2Cl_2	596, 640	588,4	23,2	4,85; 4,82	1,08	1,01	1458	1,07	2,0	0,046
	CH_3CN	584, 626	564,2	36,5	4,80; 4,66	1,39	1,06	1670	0,94	1,5	0,037
Ih	CH_2Cl_2	606, 650	608,7	11,9	4,85; 4,94	0,82	0,96	1337	1,22	2,5	0,054
	CH_3CN	596, 640	581,0	28,0	4,82; 4,79	1,07	1,03	1603	1,11	2,2	0,051

ally no effect on the position of the band. The transition from methylene chloride to acetonitrile gives rise in all cases to a shift of the absorption bands to the short-wave part of the spectra and to broadening of the bands. The latter is generally accompanied by a decrease in γ_1, γ_2, and F. Despite the fact that the positions and forms of the absorption bands of the dyes in the indicated solvents differ, the introduction of a methoxy group in any of the examined positions of the flavylium ring in both solvents gives rise to a simultaneous decrease in the deviations, band widths, and ratios of the intensities of the short-wave maxima to the long-wave maxima. The data obtained indicate that the observed effects in the absorption spectra of the investigated dyes when a methoxy group is introduced into the flavylium ring are due chiefly to a change in the vibron interactions that occur as a result of a change in the electronic asymmetry of the dyes. This is confirmed by the fact that the distance between the short-wave and long-wave absorption maxima, despite rather marked redistribution of the intensities, remains within the limits of the accuracy of their determination in this region (±1 nm), virtually constant (∿1150 ± 50 cm^{-1}), i.e., close to the frequency of the completely symmetrical vibration of the C—C bond of the chromophore in the excited state [3], which determines the contour of the long-wave bands of polymethine dyes. The contraction of the absorption bands and the decrease in the deviations and ratios of the intensities of the maxima on passing from the unsubstituted dye (Ia) to the methoxy-substituted dyes (Ib-h) constitute evidence for a decrease in the electronic asymmetry and, consequently, for weakening of the vibron interactions in the latter. This pattern in turn indicates the greater electron-donor character of the examined methoxy-substituted heterocyclic rings as compared with the unsubstituted ring. On the basis of the spectral characteristics presented in Table 1 for substituted (in the benzopyrylium ring) dyes Ib-e, one may set up a solvent-independent order in which the electron-donor character of the examined heteroresidues increases:

$$\text{no substituent} < 8 < 5 < 6 < 7.$$

As regards the dyes that are substituted in the 2', 3', and 4' positions, they form another series (also solvent-independent) in which the electron-donor character of the heteroresidues increases in the order

$$\text{no substituent} \lesssim 3' < 2' < 4'.$$

Inasmuch as in the case of dyes that are substituted in the 2', 3', and 4' positions one observes, as demonstrated in [1], a decrease in the torsion angle between the planes of the phenyl substituent and the benzopyrylium ring due to the effect of direct polar conjugation of the methoxy groups with the overall chromophore system, the investigated dyes cannot be arranged in a general order with respect to electron-donor character on the basis of the spectral characteristics presented above.

TABLE 2. 1,3,3-Trimethyl-2-[3-(methoxy-4-flavenylidene)-1-propenyl]-3H-indolium Perchorates

Compound	mp, °C	Found, %			Empirical formula	Calc., %			Yield, %
		C	H	Cl		C	H	Cl	
Ib	260—261	67,3	5,3	6,3	$C_{30}H_{28}ClNO_6$	67,5	5,3	6,7	20
Ic	251—252	67,2	5,3	6,4	$C_{30}H_{28}ClNO_6$	67,5	5,3	6,7	63
Id	256—257	67,1	5,2	6,2	$C_{30}H_{28}ClNO_6$	67,5	5,3	6,7	65
Ie	235—236	67,1	5,2	6,4	$C_{30}H_{28}ClNO_6$	67,5	5,3	6,7	30
If	230—231	(5,7)*		6,8	$C_{30}H_{28}ClNO_6$	(5,8)*		6,7	70
Ig	258—259	67,5	5,4	6,6	$C_{30}H_{28}ClNO_6$	67,5	5,3	6,7	75
Ih	247—248	67,4	5,1	6,5	$C_{30}H_{28}ClNO_6$	67,5	5,3	6,7	80

*Percentage of OCH_3.

Thus by introduction of substituents into one of the heterocyclic rings of unsymmetrical polymethine dyes one can change the electronic asymmetry of these dyes, and this makes it possible to regulate the form of their absorption bands.

EXPERIMENTAL

The moments of the absorption bands were determined by the method in [1]. The purity of the dyes was monitored by TLC on Silufol UV-254 plates by elution with nitromethane.

1,3,3-Trimethyl-2-[3-(5-methoxy-4-flavenylidene)-1-propenyl]-3H-indolium Perchlorate (Ib, Table 2). A mixture of 0.176 g (0.5 mmole) of 4-methyl-5-methoxyflavylium perchlorate [1] and 0.134 g (0.63 mmole) of 1,3,3-trimethyl-2-formylmethyleneindoline in 1.5 ml of distilled acetic anhydride was refluxed vigorously for 5-7 min, after which it was cooled and treated with ether (20-30 ml), and the precipitate was removed by filtration and purified by chromatography in chloroform on aluminum oxide with subsequent precipitation from solution in acetonitrile by means of 20% $HClO_4$.

Dyes Ic-h (Table 2) were similarly obtained using the corresponding methoxy-substituted 4-methylflavylium perchlorates, of which the 4'-methoxy-substituted compound was described in [5], whereas the rest were described in [1]. For purification, all of the dyes were recrystallized from acetic acid.

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