PYRYLOCYANINES.

22.* STYRILS DERIVED FROM METHOXY-SUBSTITUTED 4-METHYLFLAVYLIUM SALTS

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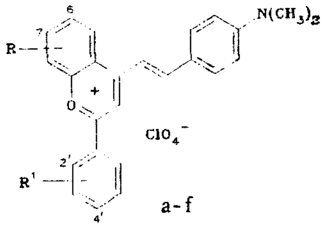
Some methoxy-substituted styrils of the flavylium series have been synthesized. Simple HMO quantum chemical calculations have shown that the terminal rings in these dyes are largely isolated in consequence of the low order of the $C_{(4)}$—$C_{(\alpha)}$ bond. The latter is responsible for and explains the unexpected effects on the positions and widths of the absorption bands consequent upon the introduction of electron-donor CH_3O groups into the heterocyclic nucleus.

Pyrylocyanine dyes containing the p-dimethylaminophenyl residue have found extensive practical application [2, 3]. For the goal-oriented synthesis of such compounds, it is necessary to establish the relationship between the chemical structures of these compounds and their spectral properties. Nevertheless, this relationship has so far been studied only with respect to absorption maxima, and only for dyes in which the heterocyclic nuclei are highly electron-donating [4-8] (F_0>45° on a 90-degree scale [9]). The aim of this study was to examine the influence of electron-donor substituents on the positions and shapes, notably the widths, of the absorption bands in styrils derived from weakly electron-donating (F_0<45°) hetero-residues. The subjects selected for study were styrils of the flavylium series, since methods for the introduction of substituents into different positions have been well developed for this residue. It is noteworthy that substituted pyrylium and benzopyrylium styrils have received little attention up to the present time.

Dyes (Ia-f) were obtained by condensing methoxy-substituted 4-methyl-flavylium salts [10, 11] with p-dimethylaminobenzaldehyde in acetic anhydride.



a-f

a,e $R=6\text{-}OCH_3$, b,f $R=7\text{-}OCH_3$; c $R^1=2'\text{-}OCH_3$, d—f $R^1=4'\text{-}OCH_3$; not shown $R, R^1=H$

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*For Communication 21, see [1].

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In Table 1, the spectral characteristics of solutions of these dyes in the weakly polar methylene chloride and the highly polar acetonitrile are compared. In view of the great differences in the shapes of the bands for styrils and the parent dyes (in the present case, flavylotrimethinecyanines and Michler's hydrol), the deviation coefficient D_M was calculated from the mean positions of the bands rather than from their λ_{max} values.

Comparison the the λ_{max} values for dyes (Ia-f) and (I) (Table 1) in the pair of solvents shows that the introduction of the electron-donor methoxy group into any of the positions tried in the heterocyclic nucleus results in a hypsochromic shift in the absorption maximum, even when similar substitution in the flavylotrimethinecyanines results in a considerable deepening in color [10, 11]. Nor do the mean positions of the bands show any tendency to deepening, except in the case of the 6-methoxystyril (Ia), the M^{-1} value of which shows a slight (∿5 nm) bathochromic shift as compared with its unsubstituted analog. It is interesting that the 4',7-dimethoxy-substituted dye (If) has approximately the same depth of color as the 7-substituted compound, although in smymmetrical flavocarbocyanines the effect of the 4'-methoxy group is clearly apparent [10, 11].

We now consider the effects of methoxy-substituents in the heterocyclic residues of styrils (Ia-f) on the breadth of the absorption bands. It will be seen from Table 1 that the dyes obtained have narrower bands than the unsubstituted styril (I). The introduction of a further methoxy-group into the oxygen-containing nucleus does not result in further narrowing of the band, but rather results in a slight increase in σ (dyes Ie and If). These changes in the positions and breadths of the absorption bands in styrils (Ia-f) are unexpected. In fact, the CH_3O group, by increasing the electron-donor capacity of the heterocyclic nucleus, modifies the electronic asymmetry of the dye molecule. An increase should result in a hysochromic shift and broadening of the band, and a decrease in the opposite changes in these spectral features [12, 13]. None of these changes, as will be seen from Table 1, was seen in the present case.

The observed differences in the spectra of the substituted styrils (Ia-f) and the unsubstituted (I) cannot be due to differing extents of solvation of these compounds, since the tendency to changes in λ_{max}, M^{-1}, and σ from (I) to (Ia-f) are the same in methylene chloride (low polarity) as in acetonitrile (highly polar). In the latter, as would be expected from its greater nucleophilicity and lower refractive index [14], the bands are only hypsochromically shifted, broaded, more symmetrical, flatter, and more diffuse (lower values of γ_1, γ_2, and F) than in the former solvent (Table 1).

Additional information can be obtained by comparing the spectral effects caused by substituting CH_3O groups into the nucleus of styril (I) with those observed when similar substitution is carried out in the terminal nuclei of the symmetrical flavylotrimethinecyanine [10, 11]. An examination of the differences in the shifts of the mean band positions ΔM_s^{-1} and ΔM_f^{-1} for unsubstituted and substituted, respectively, styrils and flavylocarbocyanines (Table 1) shows that the introduction of the CH_3O group into the same position in the hetero-residue in which it causes a deepening of color in the flavylocarbocyanine results in an increase in the hypsochromic shifts in the styrils (cf. the ΔM_s^{-1} value for dye (Ib) and the corresponding value of ΔM_f^{-1}), and in positions in which this group deepens the color of symmetrical dyes, it decreases the bathochromic shift values in styrils, or even changes the sign of ΔM_s^{-1} to positive (Table 1). Quantum chemical calculations of the electron-donor ability of the terminal nuclei in the styril (I) by the simple HMO method give a F_0 value of 24° for the flavenylidene residue, and of 11° for the p-dimethylaminophenyl residue. Bearing in mind the fact that the CH_3O group in any position of the flavylium residue increases its basicity [12], the observed differences between ΔM_s^{-1} and ΔM_f^{-1} could be due to an increase in electronic asymmetry. However, if an increase in this asymmetry were to play a major part in changes in λ_{max} and M^{-1}, the methoxy-group in any position in the hetero-residue should enhance the color. It will be seen from Table 1 that this does not occur. Consequently, the band shift behavior is to a greater extent determined by changes in the effective length of the nucleus than by increases in the electronic asymmetry of the dye. The nucleus also plays a more important part in changes in band width in these styrils. This is clearly apparent when the σ_s values of the dyes (I-If) are compared with those of the corresponding flavylotrimethinecyanines σ_f [10, 11] (Fig. 1). This comparison shows that these values vary quite regularly. The anomalous points corresponding to compounds substituted in the 2-phenyl ring may indicate differing extents of conjugation of the 2'- and 4'-methoxy groups with the chromophore in

TABLE 1. Characteristics of the Long-Wavelength Absorption Bands* of Solutions of Styrils (I) and (Ia-f)

Dye	Position of CH_3O group	Solvent†	λ_{max}, nm	lg ε	M^{-1}, nm	ΔM_{c-1} (ΔM_f^{-1} [10, 11]), nm	D_M, nm	f	σ, cm^{-1}	γ_1	γ_2	F
I	—	1	690	5,06	664,4	—	−16,5	1,02	997	1,11	2,2	0,041
		2	676	4,96	649,7	—	−15,1	1,04	1122	1,06	2,3	0,037
Ia	6	1	692	5,10	669,4	5,0 (13,6)	−14,7	1,07	918	1,08	2,4	0,036
		2	670	4,84	654,4	4,7 (12,6)	−13,5	0,74	1031	0,88	1,5	0,025
Ib	7	1	668	5,04	649,8	−14,6 (−9,0)	−6,4	0,99	950	0,82	1,9	0,021
		2	646	4,94	637,7	−12,0 (−9,1)	−7,6	0,95	1063	0,79	1,5	0,020
Ic	2′	1	686	5,05	665,4	1,0 (4,5)	−15,2	0,96	924	1,04	2,1	0,034
		2	664	4,99	652,2	2,5 (4,1)	−15,5	1,06	1093	1,04	2,3	0,033
Id	4′	1	682	5,17	663,8	−0,6 (19,3)	−6,2	1,21	886	1,08	2,3	0,036
		2	666	5,01	652,8	3,1 (17,6)	−9,4	1,07	1034	0,96	1,9	0,028
Ie	6,4′	1	684	5,13	665,2	0,8 (29,6)		1,10	940	1,12	2,7	0,035
		2	666	4,97	653,3	3,6 (26,4)	−6,0	0,99	1081	1,07	2,7	0,033
If	7,4′	1	666	5,18	646,0	−18,4 (3,8)		1,08	985	1,01	2,3	0,034
		2	645	4,95	635,1	−14,6 (5,3)	+2,2	0,99	1115	0,96	2,1	0,028

*M^{-1} is the mean position of the band measured by the method of moments; f is the oscillator strength; σ is the band width; γ_1 the asymmetry coefficient; γ_2 the excess coefficient; and F is the fine structure constant.

† 1 denotes methylene chloride, and 2, acetonitrile.

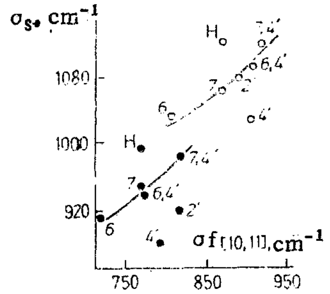

Fig. 1. Relationship between absorption band width in styrils (I-If) and the corresponding flavylotrimethinecyanines (σ_S): black circles represent methylene chloride, and light circles, acetonitrile.

symmetrical and nonsymmetrical dyes. It therefore follows from Fig. 1 that substituents introduced into the heterocyclic nucleus of styril (I) influence the extent of vibronic interactions to approximately the same extent as in symmetrical flavylocarbocyanines. In other words, the substituent has a greater effect on changes in bond order on excitation in the hetero-residue in styril (I) than in the polymethine chain. For example, when a methoxy group is introduced into the 6-position of the styril (I), the Δp contribution of all the bonds in the flavylium nucleus to the overall δ value decreases by 2.6%, whereas the contribution of all the remaining bonds remains virtually unchanged (~+0.005%).

Quantum chemical calculations for styrils (I) and (Ia), even with the same values for the resonance integrals (β_{CC} = 1) for the bonds of the polymethine chain, suggest substantial alternation in the orders of these bonds. For example, the orders of the π-bonds $C_{(4)}$—$C_{(\alpha)}$, $C_{(\alpha)}$—$C_{(\beta)}$, and $C_{(\beta)}$—$C_{(\gamma)}$ in the ground state in dye (I) have the values 0.5349, 0.7370, and 0.4844 respectively, and in (Ia) these values are 0.5344, 0.7374, and 0.4844 respectively.

TABLE 2. Properties of Styrils (Ia-f)

Dye	mp*, °C	Found, %			Empirical formula	Calculated, %			Yield, %
		C	H (OCH₃)	Cl		C	H (OCH₃)	Cl	
Ia	225		(6,4)	7,0	$C_{26}H_{24}ClNO_6$		(6,4)	7,4	75
Ib	242	64,9	4,6	7,4	$C_{26}H_{24}ClNO_6$	64,8	5,0	7,4	80
Ic	201		(6,1)	7,0	$C_{26}H_{24}ClNO_6$		(6,4)	7,4	74
Id	249		(6,1)	7,1	$C_{26}H_{24}ClNO_6$		(6,4)	7,4	80
Ie	239	63,2	5,3	6,9	$C_{27}H_{26}ClNO_7$	63,3	5,1	6,9	75
If	250	63,3	4,8	6,7	$C_{27}H_{26}ClNO_7$	63,3	5,1	6,9	65

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*Dyes (Ic, e, f) from acetic anhydride, (Ia) from a mixture of acetic and formic acids (9:1), (Ib) from a mixture of acetic acid and acetic anhdyride (1:1), and (Id) from a mixture of acetic and formic acids (3:2).

These alternations are even greater when the differences between these bonds are taken into account. For instance, if $\beta_{C_{(4)}-C_{(\alpha)}} = \beta_{C_{(\beta)}-C_{(\gamma)}} = 0.8\beta$ and $\beta_{C_{(\alpha)}-C_{(\beta)}} = 1.2\beta$ the orders of the same bonds in the styril (I) are 0.3896, 0.8602, and 0.3521, and in (Ia), 0.3893, 0.8604, and 0.3520. These calculations show that the $C_{(4)}-C_{(\alpha)}$ bond approximates to a single one. Consequently, the heterocyclic ring is to a large extent isolated from the rest of the cation. This isolation also appears to result in spectral features resulting from substitution in the heteroresidue in the styril (I) being mainly governed by changes in the electronic characteristics of the ring itself.

Further isolation of the terminal nuclei could result from rotation around the $C_{(4)}-C_{(\alpha)}$ bond. It may be pointed out immediately that conformational effects should not play an important part in differences between the unsubstituted styril (I) and its substituted derivatives (Ia-f), since the fluorescence spectra of these dyes are mirror images of the absorption spectra, and are independent of the excitation wavelength.

To summarize, it may be concluded that in the molecule of the styril (I) the terminal nuclei, which are poor electron donors, are largely isolated as a result of the low order of the $C_{(4)}-C_{(\alpha)}$ bond, which results in and is the reason for the unexpected changes in the positions and widths of the bands on introducing electron-donating CH_3O groups into the heterocyclic nuclei.

EXPERIMENTAL

Absorption band moments were measured as in [1] from the absorption spectra obtained on an SF-4A spectrophotometer. Quantum chemical calculations were carried out by the simple HMO method with the set of parameters given in [15]. The methoxy group was modeled as in [10]. The purities of the compounds were checked by TLC on Silufol UV-254 plates, with nitromethane as eluent.

4-[1-(4-Dimethylaminophenyl)-2-vinyl]-6-methoxyflavylium Perchlorate (Ia, Table 2). A mixture of 0.100 g (0.29 mmole) of 4-methyl-6-methoxyflavylium perchlorate [9], 0.043 g (0.33 mmole) of p-dimethylaminobenzaldehdye, and 1.5 ml of distilled acetic anhydride was boiled for 5 min. After cooling, the solid dye was isolated by filtration.

4-[1-(4-Dimethylaminophenyl)-2-vinyl]-7-methoxyflavylium (Ib), 4-[1-(4-dimethylaminophenyl)-2-vinyl]-2'-methoxyflavylium (Ic), 4-[1-(4-dimethylaminophenyl)-2-vinyl]-4'-methoxyflavylium (Id), 4-[1-(4-dimethylaminophenyl)-2-vinyl-4', 6-dimethoxyflavylium (Ie), and 4-[1-(4-dimethylaminophenyl)-2-vinyl]-4',7-dimethoxyflavylium (If) perchlorates were obtained as for (Ia) from the appropriate 4-methylflavylium salts [10, 11].

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REACTIVITY OF CYCLIC SULFIDES IN REACTIONS WITH QUINONES

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Sulfonium salts are obtained by the reaction of cyclic sulfides with 1,4-benzoquinone and 5,8-quinolinedione in an acidic medium. It is shown by the method of concurrent reactions that the introduction of alkyl substituents into molecules of thiacyclopentane and thiacyclohexane decreases the reactivity of the sulfides. Quinolinedione is less reactive towards sulfides than is benzoquinone.

It is known [1, 2] that sulfides in an acidic medium react with quinolines, forming sulfonium salts. There is no information in the literature concerning the special behavior in this reaction of quinones that contain a heterocyclic ring, expecially quinolinediones. Nor is there any on the effect of the structure of the sulfides on their reactivity. We were interested in studying the behavior of cyclic sulfides analogous to the sulfides in the middle fraction of petroleum, in reactions with benzoquinone and 5,8-quinolinedione. To this end we prepared sulfonium salts from sulfides IIa-j (see Table 1) and also made quantitative estimate of the reactivity of the sulfides by means of GLC. The composition and structure of the salts were proven by elementary analysis and IR and PMR spectroscopy.

During this, it was found that a basic feature of the sulfonium salts formed in reactions with 5,8-quinolinedione is that each molecule of the salt contains two anions of the acid. In the PMR spectra of these salts, a shift of the protons of the nitrogen-containing ring to weaker fields is observed, indicating the coordination of a second molecule of HCl per nitrogen atom of the heterocycle. This probably explains the fact that these salts when heated decompose at 150-180°C without melting. Physicochemical and spectroscopic methods have so far been unable to show unambiguously whether position 6 or 7 is joined to the sulfur.

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