ANALOGS OF STYRYL DYES AND THE SIMPLEST AZO DYES FROM 2-DIMETHYLAMINOTHIOPHENE

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The condensation of 2-dimethylaminothiophene with the appropriate derivatives of quaternary benzothiazole salts has give the vinylene-homologous series of dyes with the structure (I). By coupling with benzenediazonium salts, the simplest azo dyes of structure (III) have been synthesized. The influence on the absorption spectra of the replacement of a dimethylaniline nucleus in polymethine and azo dyes by a 2-dimethylaminothiophene nucleus has been investigated.

It has been reported [1] that dyes of type (I, n = 1), which are the thiophene analogs of the well-known styryl dyes (II), differ from the latter by a deeper coloration and by narrower and more intense absorption bands. The same differences have been observed between the spectra of the bisstyryl dyes and their analogs with thiophene nuclei.
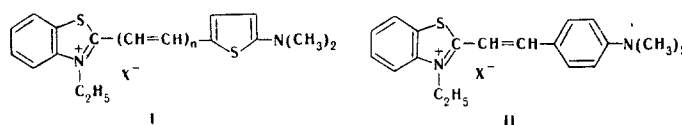
We have found that the dyes (I) can be obtained by a simpler method than that described previously [2]. 2-Dimethylaminothiophene is a more highly nucleophilic reagent than dimethylaniline [3], which enables it to be condensed with quaternary salts of 2-acetanilidovinyl derivatives of benzothiazole, and also with their vinylene homologs and with 3-ethylbenzothiazolium-2-sulfonate. In this way, we have synthesized four vinylene homologs of (I) (n = 0, 1, 2, 3). The absorption maxima, molar extinctions, and vinylene shifts of the maxima of these dyes in nitromethane solution are given in Table 1. They are all more deeply colored than the styryl dyes (II) and their vinylene homologs [4], and their absorption bands are narrower and stronger.
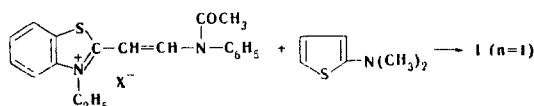

TABLE 1. Spectral Characteristics of the Dyes (I)

n	Absorption maxima, nm ($\varepsilon \cdot 10^{-5}$)	Vinylene shift, nm
0	471 (0,86)	
1	567 (1,35)	96
2	659 (1,63)	92
3	762 (1,10)	103

The reason for these differences in the spectra [1] is the greater delocalization of the π electrons of the chromophores of the dyes (I) than of the chromophores of the styryl dyes (II) and their vinylene homologs. This is also confirmed by the vinylene shifts of the maxima of the absorption bands which for the dyes (I) with thiophene nuclei, as for the symmetrical cyanines, are close to 100 nm [5], while for the dyes with a benzene nucleus (II) they are always about 40 nm [4].

* Deceased.

TABLE 2. Spectral Characteristics of the Azo Dyes (III) and (IV)

R	The dyes (III)					The dyes (IV)				
	absorp. spec. in C_2H_5OH		absorp. spec. in C_2H_5OH + HCl*		Δ, nm	absorp. spec. in C_2H_5OH		absorp. spec. in C_2H_5OH + HCl*		Δ, nm
	λ_{max}, nm	$\varepsilon \cdot 10^{-4}$	λ_{max}, nm	$\varepsilon \cdot 10^{-4}$		λ_{max}, nm	$\varepsilon \cdot 10^{-4}$	λ_{max}, nm	$\varepsilon \cdot 10^{-4}$	
OCH_3	483	4,97	503	4,98	+20	410	2,88	560	2,67	+150
H	482	4,98	474	4,99	−8	412	2,76	520	3,41	+108
NO_2	554	5,00	464	5,03	−90	480	3,30	510	6,52	+30

*One volume of concentrated HCl to nine volumes of ethanol.

TABLE 3. Analytical Characteristics of the Dyes Obtained

Com-pound	Name	Mp, °C	Empirical formula	Found, %	Calc., %	Yield, %
I $n=0$	2-(5-Dimethylamino-2-thi-enyl)-3-ethylbenzothia-zolium perchlorate	237	$C_{15}H_{17}ClN_2O_4S_2$	S 16,44	S 16,47	64
I $n=1$	2-[2-(5-Dimethylamino-2-thienyl)vinyl]-3-ethylben-zothiazolium iodide	240	$C_{17}H_{19}IN_2S_2$	I 28,78	I 28,73	80
I $n=2$	2-[4-(5-Dimethylamino-2-thienyl)buta-1,3-dienyl]-3-ethylbenzothiazolium perchlorate	211	$C_{19}H_{21}ClN_2O_4S_2$	S 14,08	S 14,52	27
I $n=3$	2-[6-(5-Dimethylamino-2-thienyl)hexa-1,3,5-trienyl]-3-ethylbenzothiazolium perchlorate	179	$C_{21}H_{23}ClN_2O_4S_2$	S 13,38	S 13,71	17
III R=OCH_3	2-Dimethylamino-5-(4-meth-oxyphenylazo)thiophene	155	$C_{13}H_{15}N_3OS$	N 16,19	N 16,09	47
III R=H	2-Dimethylamino-5-phenyl-azothiophene	124	$C_{12}H_{13}N_3S$	N 18,19	N 18,18	51
III R=NO_2	2-Dimethylamino-5-(4-nitro-phenylazo)thiophene	198	$C_{12}H_{12}N_4O_2S$	N 19,93	N 20,28	55

The coupling of 2-dimethylaminothiophene with diazonium salts takes place readily. Table 2 gives the absorption maxima and molar extinctions in ethanolic solutions of three azo dyes of the general formula (III)


III

R = OCH_3, H, NO_2
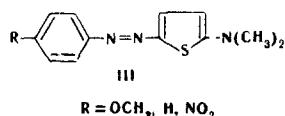
and the same characteristics for ethanolic solutions acidified with hydrochloric acid (one volume of concentrated hydrochloric acid to nine volumes of ethanol). For comparison, the figures for the analogous dyes (IV) containing a dimethylaniline nucleus are also given.


IV

R = OCH_3, H, NO_2
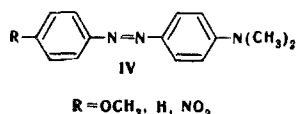
The figures of Table 2 show that in neutral ethanolic solution passage from the azo dyes (III) to the azo dyes (IV) is accompanied by a considerable shift of the absorption bands into the long-wave part of the spectrum and by an increase in their intensity. These differences in the absorption spectra of the dyes (III) and (IV) are due to the same factors as the difference in the spectra of the dyes (I) and (II) considered above.

A substantial difference between the azo dyes (III) and the azo dyes (IV) is also observed in their be-havior to hydrochloric acid. In the majority of cases, the addition of a proton to the molecule of an azo dye leads to a deepening of the color of its solution, which is connected with a rise in the energetic equiva-lence of its resonance structures [6]. However, the color of solutions of the azo dyes (III, R = H) and, par-

ticularly, (III, R = NO_2) on acidification is not deepened but is lightened (negative halochromism). This means that in the two azo dyes mentioned the resonance structures are close to equivalence in energy even in neutral ethanolic solution,
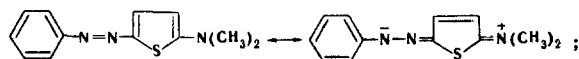
and the addition of a proton, increasing the proportion of the right-hand structure,
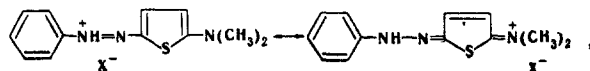
now leads not to an increase but to a decrease in the delocalization of the π electrons in their chromophores.

Unfortunately, the azo dyes (III) that we obtained show no appreciable narrowing of the absorption bands, as compared with the azo dyes (IV), either in neutral or in acid solution. Apparently we are dealing here with a specific characteristic of all azo dyes.

EXPERIMENTAL

The dyes (I) were obtained by boiling for 10 min pyridine solutions of equimolar amounts of 2-dimethylaminothiophene (V) and 3-ethylbenzothiazolium-2-sulfonate (the dye I, n = 0), and of (V) and 2-(2-acetanilidovinyl)-, 2-(4-acetanilidobuta-1,3-dienyl), and 2-(6-acetanilidohexa-1,3,5-trienyl)-3-ethylbenzo-thiazolium iodides (the dyes I, n = 1, 2, and 3, respectively). After the pyridine had been distilled off in vacuum, the dyes (I, n = 0, 2, 3) were converted into the perchlorates by the action of sodium perchlorate on methanolic solutions of the dyes, and these were crystallized from methanol. The dye (I, n = 1) was recrystallized from methanol with the addition of sodium iodide.

The azo dyes (III) were obtained by coupling the diazonium salts from p-anisidine, aniline, and p-nitroaniline with (V) in an acetate buffer with the subsequent precipitation of the azo dye with ammonia. The dyes (III, R = OCH_3 and H) were crystallized from heptane, and (III, R = NO_2) from toluene.

The names, melting points, analytical characteristics, and yields of the dyes synthesized are given in Table 3.

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