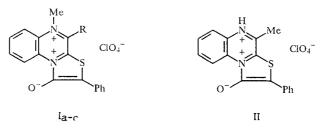# ASYMMETRIC POLYMETHINE DYES BASED ON
THIAZOLO[3,2-a]QUINOXALINIUM SALTS

K. V. Fedotov

Asymmetric carbocyanine dyes, the solutions of which are characterized by the presence of several absorption bands in the visible and near-IR regions, were synthesized from 4,5-dimethyl-1-oxo-2-phenyl-1,5-dihydrothiazolo[3,2-a]quinoxalin-3-ium perchlorate. Their deep color is due both to a more effective length of the condensed heterocyclic system and to the strong interaction of the electronic transitions, localized on the polymethine chain and on the heterocyclic ring.

In the preceding article [1], the synthesis of thiazolo[3,2-a]quinoxalinium salts (Ia-c) has been described.

The characteristic feature of their solutions is the absorption in the visible region of the spectrum (580-610 nm), in which the polymethine dyes usually absorb [2]. The methyl group at the 4-position of the quaternary thiazoloquinoxalinium salt Ib, as, for example, in the quaternary quinaldinium salts, has a nucleophilic activity which may be utilized for synthesizing polymethine dyes from them. The methyl group at the 4-position of the thiazoloquinoxalinium salt (II) displays similar activity.

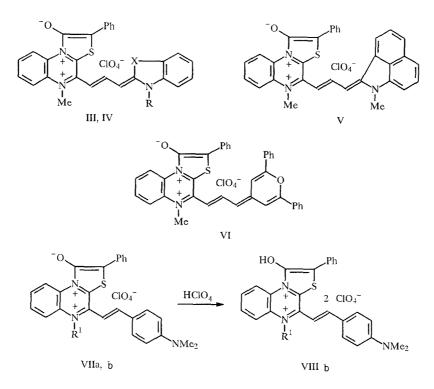Ia-c   II

I a R=H, b R=Me, c R=Ph

It was of interest to synthesize similar dyes from salt Ib, especially since, according to theoretical considerations, the thiazolo[3,2-a]quinoxalinium ring has a considerably longer effective length [3] (L = 8.78) than most of the heterocyclic systems used in the synthesis of polymethine dyes. For this reason, these dyes should have a relatively deep color. It could be expected that this effect will be even greater because of the interaction of electronic transitions localized on the atoms of the heterocyclic and polymethine chromophoric systems.

To synthesize these dyes, salt Ib was condensed with formylmethylene derivatives of several heterocyclic compounds. In this way, new asymmetric cyanines III-VI were synthesized. It must be emphasized that the dyes are formed only with formylmethylene derivatives of heterocyclic compounds. With 4-dimethylaminobenzaldehyde styryl dyes VIIa, b were obtained, so that for the preparation of styryl VIIa, salt II was used (see below).

The solutions of the synthesized dyes are characterized in the visible and near-IR regions of the spectrum, generally by three absorption bands (Table 1). In addition to the band positioned in the absorption region of the initial salt Ib (~588 nm), two further bands are usually observed, one of which is located in a longer-wave region with respect to it (667-808 nm) and the other in the shorter-wave region (375-518 nm). On comparison of the maxima of the long-wave absorption bands of the asymmetric dyes III-V, VIIb (see Table 1) with the corresponding characteristics [4-6] of their spectral analogs containing a quinaldinium residue, the effective length of which is considerably shorter (L 3.23), it is seen that the introduction of the mesoionic fragment leads to a substantial bathochromic shift of this band (125-173 nm).

The presence in the visible part of the spectrum of two or more absorption bands may be due to the presence of several chromophoric systems in the molecule of the dye [7]. In the dyes studied two such systems can be conditionally isolated. One of these is the polymethine chain proper, and the other a conjugated system of the mesoionic heterocyclic ring localized mainly on the atoms of the thiazole fragment [1]. As in the case of biscyanines [7], the interaction of these chromophores should lead

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III X = CMe₂, R = Me; IV X = S, R = Et; VII a R¹ = H, b R¹ = Me

to separation of their absorption bands. The interacting bands are thus shifted more strongly the closer the energetic levels of their transitions are located. The degree of the interaction (Δ) of these levels is calculated from the following equation [8]:

$$|\Delta| = (\lambda_1 - \lambda_2) - |\lambda_{par}^{1} - \lambda_{par}^{2}|$$

where λ_1 and λ_2 are the maxima of the long-wave and short-wave bands of the dye; $|\lambda_{par}^{1} - \lambda_{par}^{2}|$ is the absolute value of the difference of the maxima of the long-wave absorption bands of the starting "parent" dyes.

The absorption maximum of the initial salt Ib can be accepted as the absorption maximum of the "parent" chromophore, localized on the thiazoloquinoxalinium atoms.

The absorption maximum of the second "parent" chromophore can be determined in two ways. The simplest method is to use the absorption maxima of their structural analogs based on the quinaldinium salt. This path is very approximate in view of the strong differences of the electron-donor characters of the rings of salt Ib (30°) and quinaldine (66°).

The values of the degree of interaction of the chromophoric systems (Δ_1) for dyes III-V, VIIb calculated from these data according to the formula are given in Table 1.

TABLE 1. Characteristics of the Synthesized Compounds II-VII

Com-pound	mp, °C	λ_{max} (log ε) in CH₃CN, nm			$\Delta\lambda = \lambda_1-\lambda_2$, nm	Δ_1,nm	λ_{max}(log ε) in CH₃CN + HClO₄, nm		Δ, nm
		λ_3	λ_2	λ_1			λ_2	λ_1	
II	233 (exptl.)	—	—	582 (4,41)	—	—	—	462	—
III	194...196	434 (4,33)	582 (4,39)	734 (4,53)	152	125	—	594	151
IV	206...208	442 (4,50)	580 (4,43)	703 (4,61)	123	113	399 (3,88)	600 (4,56)	111
V	247...248	513 (4,21)	613 (4,10)	808 (4,51)	195	125	—	604 (4,30)	179
VI	272...273	465 (4,20)	648 (4,27)	780 (4,38)	132	—	—	639	118
VIIa	257...258	—	560 (4,39)	714 (4,07)	154	—	430 (4,25)	620 (4,46)	122
VIIb	231...232	374 (4,29)	576 (4,49)	667 (4,30)	89	30	400 (4,13)	602 (4,48)	77

The second path is the "detachment" of one of the chromophores by the action of strong acid on the dye solution [9]. For this purpose, the solutions of dyes III-VII in acetonitrile were protonated by 45% perchloric acid. The first and second long-wave absorption bands thereby disappear in the absorption spectrum, and a new band appears located between them. The data obtained are given in Table 1.

To find out at which of the chromophores the addition of the proton takes place, the protonation of the initial salt Ib was studied. The color of its solution was thus shifted to the short-wavelength region (456 nm). In this region the solution of the protonated dye VIIb also has an absorption band (400 nm), which probably indicates a protonation of the mesoionic fragment in cation VIIIb. During the protonation of styryl VIIa, synthesized from salt II, this band coincides even more with the band of the protonated salt Ib (430 nm).

Thus, by carrying out the protonation it is possible to "detach" the chromophore localized in the atoms of the mesoionic heterocyclic ring and to evaluate the absorption of the second "parent" chromophore.

On the basis of the data obtained, the degree of interaction (Δ) of the electronic transition localized on the polymethine chain and the mesoionic heterocyclic ring atoms was calculated according to the formula for dyes III-VII.

The data presented in Table 1 (Δ) show that the highest degree of interaction of the chromophores is observed in cyanine V with a benz[c,d]indole ring (179 nm), and the lowest — in the dye — styryl VIIb (77 nm). Thus, the degree of interaction of the polymethine and mesoionic chromophores is strongly influenced by the electron-donor character of the second hetero residue. In other words, in this case, as in biscyanines [10], the greatest interaction is observed in cyanines containing hetero residues with a similar electron-donor character. In the case of asymmetric dyes containing hetero residues, both basic and less basic than thiazoloquinoxalinium Ib, a decrease in the interaction strength of these two chromophoric systems is observed.

EXPERIMENTAL

The electronic spectra were recorded on a Specord M-400 spectrophotometer in acetonitrile. The characteristics of the synthesized compounds are given in Table 1.

The data of the elemental analyses for N, S, and Cl correspond to the calculated values. The synthesis of compounds Ib and VIIb was described in [1].

5-Methyl-2-phenylthiazolo[3,2-a]quinoxalinium-1-oxide Perchlorate (II, $C_{17}H_{13}ClN_2O_5S$). A 0.2-ml portion (3 mmoles) of 70% perchloric acid was added dropwise to a solution of 0.29 g (1 mmole) of 5-methyl-2-phenylthiazolo[3,2-a]quinoxalinium-1-oxide [11] in 10 ml of acetonitrile. The product that separated out was filtered off, washed with acetonitrile and ether, and crystallized from acetonitrile. Yield 0.37 g (74%).

5-Methyl-1-oxo-4-[3-(1,3,3-trimethyl-2(1H,3H)-indolylidene-1-propenyl]-2-phenyl-1,5-dihydrothiazolo[3,2-a]quinoxalin-3-ium Perchlorate (III, $C_{31}H_{28}ClN_3O_5S$). A mixture of 0.1 g (0.25 mmole) of perchlorate Ib and 0.05 g (0.25 mmole) of 1,3,3-trimethyl-2-formylmethylene-3H-indoline [12], and 2 ml of acetic anhydride was heated to boiling. After cooling, the precipitated dye was filtered off, washed with ethanol and ether, and crystallized from acetic acid. Yield 0.04 g (28%).

5-Methyl-1-oxo-4-[3-ethyl-2(3H)benzothiazolyidene)-1-propenyl]-2-phenyl-1,5-dihydrothiazolo[3,2-a]quinoxalin-3-ium perchlorate (IV, $C_{29}H_{24}ClN_3O_5S_2$) was obtained from 0.2 g (0.5 mmole) of perchlorate Ib and 0.1 g (0.5 mmole) of 3-ethyl-2-formylmethylenebenzothiazole [12] in 5 ml of acetic anhydride, similarly to dye III. Yield 0.15 g (51%).

5-Methyl-1-oxo-4-[3-(1-ethyl-2(1H)-benzo[c,d]indolylidene)-1-propenyl]-2-phenyl-1,5-dihydrothiazolo[3,2-a]quinoxalin-3-ium perchlorate (V, $C_{34}H_{26}ClN_3O_5S$) was obtained from 0.2 g (0.5 mmole) of perchlorate Ib and 0.11 g (0.5 mmole) of 1-methyl-2-formylmethylene-1H-benzo[c,d]indoline [13] in 5 ml of acetic anhydride, similarly to dye III. Yield 0.15 g (49%).

5-Methyl-1-oxo-4-[3-(2,6-diphenyl-4(1H)-pyrylidene)-1-propenyl]-2-phenyl-1,5-dihydrothiazolo[3,2-a]quinoxalin-3-ium perchlorate (VI, $C_{37}H_{27}ClN_2O_6S$) was obtained from 0.41 g (1 mmole) of perchlorate Ib and 0.27 g (1 mmole) of 2,6-diphenyl-4-formylmethylene-1H-pyran [14] in 15 ml of acetic anhydride, similarly to dye III. Yield 0.23 g (34%).

1-Oxo-4-(4-dimethylaminostyryl)-2-phenyl-1,5-dihydrothiazolo[3,2-a]quinoxalin-3-ium perchlorate (VIIa, $C_{26}H_{22}ClN_3O_5S$) was obtained from 0.145 g (0.5 mmole) of salt II and 0.075 g (0.5 mmole) of 4-dimethylaminobenzaldehyde in 5 ml of acetic anhydride, similarly to dye III. Yield 0.12 g (19%).

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