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Abstract

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On Polymethine Dyes Derived from Substituted Thiazolines

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Substituents in the hetero-residues of cyanine dyes and of dyes closely related to them in structure, when conjugated with the principal chromophore, cause a considerable deepening of the color of these compounds. This bathochromic shift usually increases with an increase in the polarity of the substituents introduced (1,2), and its magnitude is evidently determined mainly by the conjugation effect. The inductive influence of substituents on the coloration of such dyes has scarcely been studied. It has only been shown that the presence of ammonium groups in the 5,5′- and 6,6′-positions of thiacarbocyanines (3,4), as well as of electron-donor groupings not conjugated with the nitrogen atoms in 2,2′-chino- (5) and indocarbocyanines (6), causes only a very small bathochromic shift of the absorption maximum of the dyes. The study, in such dyes, of the actual inductive influence of substituents on coloration is difficult, especially because of their remoteness from the principal chromophore. It therefore seemed of interest to investigate polymethine dyes derived from substituted thiazolines (Δ2) (cf. (7,8)), in which the groupings in the hetero-residues are not conjugated with the principal chromophore.

In connection with this, dyes of structures I and II were prepared, containing methyl or phenyl groups in the thiazoline residues, with inductive effects differing in sign, and their absorption spectra were investigated.

(I) $n = 1, 2, 3$

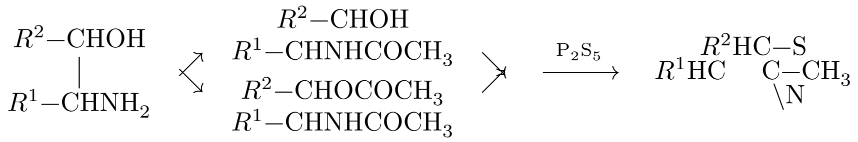
R^1	R^2
CH_3	H
H	CH_3
CH_3	CH_3
C_6H_5	H
H	C_6H_5
C_6H_5	C_6H_5

(II)

It may be assumed that in these dyes the five-membered thiazoline ring has a structure sufficiently close to planar. Therefore the spatial arrangement of the groups R^1 and R^2, located at tetrahedral carbon atoms and lying outside the plane of the hetero-residues, should not change appreciably as a result of their interaction and under the influence of substituents at the cyclic nitrogen atoms, as occurs in substituted thiazolocarbocyanines (III) ($^{9-11}$).

(III)

2,4- and 2,5-dimethyl-(^{12,13}) and 2,4,5-trimethylthiazolines (^{13}), 2-methyl-4- and 5-phenyl- and 2-methyl-4,5-diphenylthiazolines (^{14}) were obtained by the action of phosphorus pentasulfide on the mono- or diacetyl derivatives of the corresponding aminomercaptans in benzene or xylene on heating (cf. (^{13,15})).



$$\begin{array}{c} R^2\text{–CHOH} \\ | \\ R^1\text{–CHNH}_2 \end{array} \begin{array}{c} \nearrow \\ \searrow \end{array} \begin{array}{c} R^2\text{–CHOH} \\ R^1\text{–CHNHCOCH}_3 \\ R^2\text{–CHOCOCH}_3 \\ R^1\text{–CHNHCOCH}_3 \end{array} \begin{array}{c} \searrow \\ \nearrow \end{array} \xrightarrow{P_2S_5} \begin{array}{l} \;R^2\text{HC–S} \\ R^1\text{HC}\quad\text{C–CH}_3 \\ \qquad\quad\backslash\text{N} \end{array}$$

From the ethyl *p*-toluenesulfonates of these bases, symmetric carbo-, di-, and tricarbocyanines (I, $n = 1, 2, 3$) were synthesized by the usual methods.

Table 1

R^1	R^2	Thiazolinocyanines λ_{max}, mμ, $n = 1$	Thiazolinocyanines λ_{max}, mμ, $n = 2$	Thiazolinocyanines λ_{max}, mμ, $n = 3$	A for thiazolinocarbocyanines (±0.05)	Thiazolocarbocyanines (III) λ_{max}, mμ (^{9})	A for thiazolocarbocyanines (±0.05) (^{9})
H	H	445^1	545^2	650^3	3.10	543	$9.6 \cdot 10^{-3}$
CH_3	H	447	547	652	3.00	556	$5.7 \cdot 10^{-3}$
H	CH_3	446	547	652	3.15	553	$6.0 \cdot 10^{-3}$
CH_3	CH_3	448	550	656	3.60	563	$2.4 \cdot 10^{-3}$
C_6H_5	H	454	550	658	4.85	559	$5.0 \cdot 10^{-2}$
H	C_6H_5	452	555	661	4.55	592	$2.1 \cdot 10^{-1}$

R^1	R^2	Thiazolinocyanines λ_{max}, mμ, $n = 1$	Thiazolinocyanines λ_{max}, mμ, $n = 2$	Thiazolinocyanines λ_{max}, mμ, $n = 3$	A for thiazolinocarbocyanines (±0.05)	Thiazolocarbocyanines (III) λ_{max}, mμ (9)	A for thiazolocarbocyanines (±0.05) (9)
C_6H_5	C_6H_5 (14)	458	564	672	6.25	588	$1.8 \cdot 10^{-1}$

Literature data. In CH_3OH: ^{1} 443.5 mμ (17), 445 mμ (18); ^{2} 545 mμ (19); ^{3} 645 mμ (20).

Dimethinemerocyanines (II) were obtained by interaction of the indicated quaternary salts with 3-ethyl-5-ethoxymethylenerhodanine in absolute ethyl alcohol in the presence of triethylamine. In most cases the dyes were purified by chromatography on aluminum oxide to separate by-products (in particular, neocyanines in the synthesis of carbocyanines), followed by crystallization. In the synthesis of merocyanines (II), among the by-products there was observed the formation of a monomethinoxanine derivative of 3-ethylrhodanine, as well as more deeply colored salt-like dyes, the structure of which is being studied.

Table 2

R^1	R^2	λ_{max}, mμ	Hypsochromic shift, mμ
H	H	482*	11.5
CH_3	H	483	11.5
H	CH_3	483	11
CH_3	CH_3	484	11
C_6H_5	H	482	16
H	C_6H_5	484	13
C_6H_5	C_6H_5	484	16

* Literature data: 482.5 mμ (in CH_3OH) (22); 482 mμ (in C_2H_5OH) (23).

Table 1 gives the positions of the absorption maxima (λ_{max}) in alcoholic solutions of substituted thiazolinocyanines (I, $n = 1, 2, 3$) and the corresponding thiazolocarbocyanines (III) (measured on an SF-2 spectrophotometer), and, for dyes I ($n = 1$) and III, also the values A (16), characterizing their basicity.

From the data of Table 1 it is seen that the introduction of methyl groups into the hetero residues of thiazolinocyanines has very little effect on the position of the absorption maximum of the dyes and on the magnitude of their basicity; phenyl radicals in the same positions cause a somewhat greater deepening of color and a marked decrease in the basicity of the dyes. Analogous substitution in the thiazolocarbocyanine molecule leads to significantly larger bathochromic shifts of the absorption maximum (13–49 mμ) and changes in basicity (^{9}). The influence of substituents in the 4,4′- and 5,5′-positions on the color of thiazolinocarbocyanines is practically identical and additive. At present

It is difficult to explain the somewhat reduced basicity of 4,5,4′,5′-tetramethylthiazolinocarbocyanine; it seems unlikely that the introduction of methyl groups causes such a distortion of the valence angles of the thiazoline ring as could affect the basicity of the dye.

Table 2 gives the absorption maxima of the synthesized dimethylmerocyanines II and the values of the "hypsochromic shifts" (21), calculated for these dyes.

The data of Table 2 confirm that only in the case of the introduction of phenyl groups does some lowering of the basicity of the thiazoline heteroresidue occur.

Thus, using cyanine and merocyanine dyes derived from thiazoline as examples, it has been shown that the introduction into the heteroresidue of substituents not conjugated with the principal polymethine chromophore and, consequently, possessing only an inductive effect, has very little influence on the color and, in some cases, on the basicity of the dyes. In the case of methyl groups $(+J_{\text{effect}})$, this influence is manifested more weakly than in the case of phenyl groups $(-J_{\text{effect}})$. It is still unclear whether these differences are connected only with the direction or also with the magnitude of the inductive effects of these substituents.

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