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Abstract

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On Merocyanine Dyes with Electron-Donating Substituents in the Polymethine Chain

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Of the merocyanine dyes substituted in the chain ([1–4]), only dimethinemerocyanines—rhodanine derivatives with an alkyl or phenyl group in the polymethine chromophore—have been studied sufficiently ([1,4a]).

In this connection, it was of interest to study methods of synthesis and the properties of di- and tetramethinemerocyanines containing an electropositive substituent in the α-position, for example an alkoxy, amino, or substituted amino group (I).

I II III

where Z is a heterocyclic residue; $A = OR$, NH_2, NHR', NC_5H_{10}, or $NR'COCH_3$; $R = CH_3$ or C_2H_5; $R' = H$, an alkyl, benzyl, or phenyl group; $B = OCH_3$, SCH_3, or $C_6H_5NCOCH_3$; $n = 0$ or 1; $\overline{X}$ is an acid residue.

By the interaction of 3-ethyl-5-(α-ethoxyethylidene)rhodanine ([5]) (II, $R = C_2H_5$) with ethyl p-toluenesulfonate of 2-ethylmercaptobenzothiazole in an alcoholic medium in the presence of triethylamine at ordinary temperature, α-ethoxydimethinemerocyanine was obtained (I, $A = OC_2H_5, n = 0, Z =$ benzothiazole residue; bright-red needles with m.p. 154°).

Found, %: N 7.09; 7.06

$C_{18}H_{20}O_2N_2S_3$. Calculated, %: N 7.13 (cf. [2a]).

Analogously, α-ethoxy-substituted dimethinemerocyanines were synthesized with residues of 6,7-tetramethylbenzothiazole, benzoselenazole, quinoline (2), benzoxazole, and thiazoline; in the case of benzoxazole and thiazoline derivatives the reaction was carried out in acetic anhydride in the presence of triethylamine upon heating.

Further, by condensation of 3-ethyl-5-(α-ethoxyethylidene)rhodanine (II, $R = C_2H_5$) with quaternary salts of vinyl derivatives of heterocyclic bases containing the readily detachable group III, in a solution of ethyl alcohol or acetic anhydride in the presence of triethylamine, we succeeded in obtaining α-ethoxytetramethinemerocyanines (I, $A = OC_2H_5, n = 1$) with residues of benzothiazole (dark-blue lustrous needles with m.p. 160°).

Found, %: N 6.51
$C_{20}H_{22}O_2N_2S_3$. Calculated, %: N 6.69, ([11]),

as well as benzoselenazole and 3,3-dimethylindolenine.

It could be expected that in these dyes (I, A = OR) the alkoxy group, just as in 3-ethyl-5-(α-ethoxyethylidene)rhodanine ([5]), cf. also ([6–8]), would possess considerable mobility and, in particular, the ability to be exchanged for an amine residue, which would give us the possibility of passing from these compounds to the previously undescribed α-amino-substituted merocyanines.

Indeed, on heating for 1 hour α-ethoxy- or α-methoxydimethinemerocyanine—a benzthiazole derivative—with an excess of ethylamine (30 moles per mole of dye) in alcoholic solution, the color of the latter increased sharply. In both cases dyes identical in their properties were isolated in good yield; their elemental composition indicates that they are merocyanines with an ethylamino group in the α-position (light-yellow needles, m.p. 167°).

Found, %: N 10.52
$C_{18}H_{21}ON_3S_3$. Calculated, %: N 10.70

The reaction proceeded in exactly the same way with methyl-, *n*-butyl-, *n*-nonyl-, *n*-dodecyl-, and benzylamines.

Quite analogously (by the action of ethylamine on the corresponding α-ethoxymerocyanines), α-ethylamino-substituted dimethinemerocyanines were synthesized with residues of 6,7-tetramethylbenzthiazole, benzoselenazole, quinoline (2), and thiazoline, as well as tetramethinemerocyanine (I, $A = NHC_2H_5, n = 1$)—a benzthiazole derivative (dark-red needles, m.p. 146°).

Found, %: N 9.84
$C_{20}H_{23}ON_3S_3$. Calculated, %: N 10.06.

Exchange of the ethoxy or methoxy group in merocyanines of structure I (A = OR) also occurs at ordinary temperature, but the reaction proceeds considerably more slowly. Under these conditions, by interaction for 15 days of α-ethoxymerocyanine, a benzthiazole derivative, with ammonia in alcoholic solu-

tion, we succeeded in obtaining an α-amino-substituted dye (I, $A = NH_2, n = 0$; orange prisms, m.p. 227°).

Found, %: N 11.57

$C_{16}H_{17}ON_3S_3$. Calculated, %: N 11.56

Heating in this case leads to a number of side processes.

The reaction of α-ethoxydimethinemerocyanine—a benzthiazole derivative—with aniline and with secondary amines proceeds quite differently. When it is heated with 30 moles of piperidine without solvent at 100°, or in boiling ethyl alcohol, only traces of the α-*N*-piperidyl-substituted dye are formed, and the principal reaction product is a yellow substance (m.p. 198°, absorption maximum at λ 441 mμ), which, unlike merocyanines, is strongly adsorbed on aluminum oxide and dissolves with difficulty in nonpolar solvents. The dye with a piperidine residue in the α-position was obtained in small yield by heating α-methylmercaptodimethinemerocyanine with piperidine at 100°.

With aniline and diethylamine, under the conditions indicated above, substitution of either the ethoxy or the methylmercapto group has so far not been achieved.

IV

V

where $A = NH_2$, $NHCH_3$, NHC_2H_5, NHC_6H_5 or NC_5H_{10}; $R = H$, C_2H_5 or C_6H_5.

Meanwhile, it turned out that 3-ethyl-5-(α-ethoxyethylidene)rhodanine (II, R = C_2H_5) reacts with aniline and piperidine just as readily as with ammonia and primary aliphatic amines (for example, with methyl- or ethylamine) ([5]), with the formation of amino-substituted ethylidenerhodanines (IV).

As in the quaternary salts of β-alkoxypropenyl derivatives of heterocyclic bases ([6]), replacement of the ethoxy group in α-ethoxyethylidenerhodanine (II, R = C_2H_5) by the residue of an aliphatic amine leads to a sharp decrease in the reactivity of the methyl group in these compounds. However, this phenomenon is manifested to a noticeably smaller extent in the case of 3-ethyl-5-(α-phenylaminoethylidene)rhodanine (IV, A = NHC_6H_5). By condensation of the latter with the ethyl-*p*-toluenesulfonate of 2-ethylmercaptobenzthiazole we succeeded in obtaining α-phenylaminodimethinemerocyanine with a benzthiazole residue (I, $n = 0$, A = NHC_6H_5).

Table 1

A	λmax, mμ	Shift of absorption maximum, mμ
$n = 0$		
H	524(1)	–
C_2H_5	536(1)	+12
CH_3O	519	−5
C_2H_5O	521	−3
NH_2	467	−57
CH_3NH	452	−72
C_2H_5NH	454	−70
n-C_4H_9NH	453	−71
n-$C_9H_{19}NH$	451	−73
n-$C_{12}H_{25}NH$	452	−72
$C_6H_5CH_2NH$	455	−69
C_6H_5NH	499	−25
$C_5H_{10}N$	471	−51
$NHCOCH_3$	542	+18
$C_2H_5NCOCH_3$	541	+17
$C_6H_5NCOCH_3$	545	+21
$n = 1$		
H	607(9)	–
CH_3O	607	0
C_2H_5O	607	0
C_2H_5NH	520	−87

As was to be expected, acetylation of the amino group in compounds IV leads to a noticeable increase in the mobility of the hydrogen atoms of the methyl group. Thus, on heating 3-ethyl-5-(α-aminoethylidene)rhodanine (IV, A = NH_2) with the ethyl-*p*-toluenesulfonate of 2-ethylmercaptobenzthiazole in a mixture of pyridine and acetic anhydride in the presence of triethylamine, dimethinemerocyanine containing an acetamino group in the α-position is formed (V, R = H; dark-red prisms with m.p. 236°).

Found, %: N 10.31
$C_{18}H_{19}O_2N_3S_3$. Calculated, %: N 10.36

Similarly, starting from the corresponding ethylidenerhodanines (IV, A = NHC_2H_5 or NHC_6H_5), α-ethylacetamino- and α-phenylacetamino-merocyanines (V, R = C_2H_5 or C_6H_5) were synthesized. It was further shown that dyes of structure V can also be obtained by acetylation of the corresponding α-amino-, α-ethylamino-, and α-phenylaminomerocyanines.

The absorption maxima of the synthesized di- and tetramethinemerocyanines (I) with a benzthiazole residue, as well as of several other dyes of this group, are given in Table 1 (in C_2H_5OH).

As already noted earlier ([1]), introduction into the α-position of the polymethine

chain of the weakly electropositive ethyl group causes a shift of the absorption maximum to the long-wavelength region. As the electron-donating character of the substituent (A) increases, as can be seen from Table 1, a hypsochromic shift is observed, especially sharply expressed in the alkylamino-substituted compounds (69–73 mμ); the magnitude of this shift is appreciably greater in the tetramethinemerocyanine ($n = 1$, 87 mμ).

A similar change in the position of the absorption maximum upon introduction of alkoxy and ethylamino groups also occurs in merocyanines with residues of 6,7-tetramethylbenzthiazole, benzoselenazole, quinoline ([2]), and thiazoline.

The intensification of color upon introduction into the α-position of merocyanines of strongly electropositive substituents is apparently explained by electron displacements from these groups toward the carbonyl oxygen of the rhodanine residue. The resulting formation of a new positively charged center and, as a consequence, a decrease in the uniformity of the distribution of electron-

···of density in the principal chromophoric system leads, as in the case of thiacarbocyanine[8] and triphenylmethane[10] dyes, to a deepening of the color.

In accordance with this, acetylation of the amino group entails a sharp bathochromic shift of the absorption maximum of the dyes (see Table 1); the acetyl group, by withdrawing electrons from the nitrogen atom of the amino group, thereby decreases the electron displacement from this substituent toward the carbonyl oxygen of the rhodanine residue.

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Note: Figure translations are in progress. See original paper for figures.