# *Some Dyes derived from 2-Hydroxymethylbenzothiazole.*

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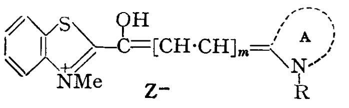
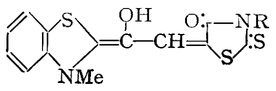
Preparations defined in the title are described.

ZUBAROVSKI (*J. Gen. Chem., U.S.S.R.*, 1951, **21**, 2055) has described a number of derivatives of hydroxymethylbenzothiazole, including the quaternary salt ethiodide. He stated, however, that owing to certain difficulties he was unable to isolate cyanine dyes with a hydroxyl substituent in the polymethin chain. This paper describes the preparation and properties of several of these dyes.

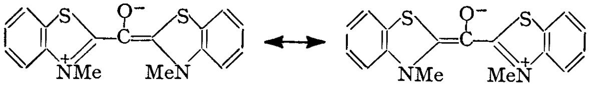
When 2-hydroxymethyl-3-methyl- and 3-methyl-2-methylthio-benzothiazolium toluene-*p*-sulphonate were refluxed together in ethanol with 1 mol. of triethylamine, an orange dye crystallized, whose empirical formula corresponded to (I; A = benzothiazoline, *m* = 0, R = Me, Z = $C_6H_4Me{\cdot}SO_3$). The solution in aqueous ethanol was cerise, in pyridine purple, and in ethanol with a drop of triethylamine it was blue. All of these solutions slowly faded and became colourless. It is probable that the deep colour in basic solutions was due to the degenerate zwitterionic resonance system (I*a*) ↔ (I*b*), wherein any structure such as (I*c*) is prohibited by the adjacent negative charges.



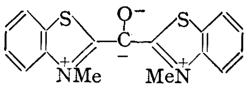
(I)



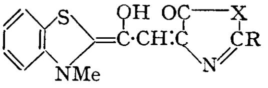
(II)



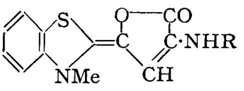
(I*a*) (I*b*)



(I*c*)



(III)



(IV)

A trimethincyanine was prepared from the hydroxymethyl quaternary salt and 2-2′-acetanilidovinyl-3-ethylbenzoxazolium iodide with 1 mol. of base. This dye (I; A = benzoxazoline, *m* = 1, R = Et) was orange-red ($\lambda_{max.}$ 520 mμ) in ethanol, and addition of a drop of triethylamine produced a transient green colour.

Two *mero*cyanine dyes (II; R = $CH_2{\cdot}CH{:}CH_2$ and R = $CH_2{\cdot}CO_2Et$) possessing a thiazolid-4-one ring were prepared from the appropriate 5-ethoxymethylene intermediates. These dyes were magenta ($\lambda_{max.}$ 560 mμ) in ethanol, and basification produced a transient blue colour, quickly fading to colourless. The dyes were easily acetylated to the *mero*cyanines with an acetoxy-group on the chain, which had absorption maxima similar to dyes with unsubstituted chains.

A common property of all of these dyes is their rapid decomposition in basic solutions, although before completely decomposing they exhibit the deep colours pertaining to dyes with $O^-$ in the chain.

When the 2-hydroxymethyl quaternary salt and 4-ethoxymethylene-2-ethylthiothiazol-5-one were condensed in the presence of a base the initial colour of the solution was magenta. However, this colour quickly became degraded and only a yellow dye having $\lambda_{max.}$ 470 mμ was isolated. The analogous dye from 4-ethoxymethylene-2-phenyloxazol-5-one was also yellow ($\lambda_{max.}$ 467 mμ), and neither of these dyes was affected by alkali, although their analyses were similar to those for the hydroxy-dyes. By analogy with the structures of the thiazolid-4-one *mero*cyanines it may be deduced that the initial dyes formed were

(III; X = S, R = SEt) and (III; X = O, R = COPh), the former being responsible for the observed magenta colour. It is also known that the thiazolone and oxazolone rings present in these dyes are easily opened at the $C_{(5)}$–S and $C_{(5)}$–O bonds (Cook *et al.*, *J.*, 1948, 1056, 1060) providing carboxylic acids, esters, and amides. These intermediates formed from (III) are γ-hydroxy-ketones, which may cyclize to the lactones (IV; R = $CS_2Et$, COPh). The latter structures account for the properties including the similar absorption spectra, of these dyes.

## EXPERIMENTAL

2-Hydroxymethyl-3-methylbenzothiazolium toluene-*p*-sulphonate was prepared from 2-hydroxymethylbenzothiazole (Zubarovski, *loc. cit.*) (1·65 g.) and methyl toluene-*p*-sulphonate (1·86 g.) on the steam-bath during ¼ hr. The product solidified.

*Bis-(3-methyl-2-benzothiazole)hydroxymethincyanine Toluene-*p*-sulphonate.*—2-Hydroxymethyl-3-methylbenzothiazolium toluene-*p*-sulphonate (3·51 g.) and 3-methyl-2-methylthiobenzothiazolium toluene-*p*-sulphonate (3·67 g.) with triethylamine (1·4 c.c.) in ethanol (10 c.c.) were heated for 10 min. on the steam-bath. The *dye* was filtered off and recrystallized from methanol–ether as orange needles (2·5 g.), m. p. 200° (Found: N, 5·6; S, 19·3. $C_{24}H_{22}O_4N_2S_3$ requires N, 5·6; S, 19·4%). It had $\lambda_{max.}$ in MeOH at 490 mμ, and addition of triethylamine produced a blue solution, $\lambda_{max.}$ 596 mμ.

[3-(3-*Ethyl*-2-*benzoxazole*)][1-*hydroxy*-1-(3-*methyl*-2-*benzothiazole*)] *trimethincyanine Perchlorate*.—2-Hydroxymethyl-3-methylbenzothiazolium toluene-*p*-sulphonate (3·51 g.) and 2-2′-acetanilidovinyl-3-ethyl benzoxazolium iodide (4·34 g.) with triethylamine (1·4 c.c.) in ethanol (15 c.c.) were refluxed for ½ hr. The cooled solution was poured into aqueous sodium perchlorate. An oil formed which slowly solidified. It recrystallized from pyridine–ethanol–ether as maroon leaflets, m. p. 208° (decomp.) (Found: H, 5·3; N, 5·8; S, 6·6. $C_{20}H_{19}O_6N_2ClS,EtOH$ requires H, 5·0; N, 5·6; S, 6·5%). The orange-red solution in ethanol, which had $\lambda_{max.}$ at 520 mμ, slowly changed to green with a drop of triethylamine, its absorption maxima becoming 462 mμ and 583 mμ.

3-*Allyl*-5-[2-*hydroxy*-2-(3-*methylbenzothiazolin*-2-*ylidene*)*ethylidene*]-2-*thiothiazolid*-4-*one*.—2-Hydroxymethyl-3-methylbenzothiazolium toluene-*p*-sulphonate (3·51 g.) and 3-allyl-5-ethoxymethylene-2-thiothiazolid-4-one (2·27 g.) with triethylamine (1·4 c.c.) in ethanol (15 c.c.) were refluxed for 5 min. The *dye* was filtered off and recrystallized from pyridine–methanol as a dark green powder (3·7 g.), m. p. 184° (Found: H, 4·2; N, 7·6; S, 26·7. $C_{16}H_{14}O_2N_2S_3$ requires H, 3·9; N, 7·7; S, 26·5%). An ethanol solution of the dye was magenta and had $\lambda_{max.}$ at 560 mμ. Addition of a drop of triethylamine to the solution produced an evanescent turquoise colour.

3-*Ethoxycarbonylmethyl*-5-[2-*hydroxy*-2-(3-*methylbenzothiazolin*-2′-*ylidene*)*ethylidene*]-2-*thiothiazolid*-4-*one*.—This *dye* was prepared similarly, by using 3-ethoxycarbonylmethyl-5-ethoxymethylene-2-thiothiazolid-4-one (2·75 g.). It recrystallized from pyridine–methanol as purple leaflets (3·4 g.) which darkened from 176 to 190°, with indeterminate melting or decomp. point (Found: N, 6·9; S, 23·7. $C_{17}H_{16}O_4N_2S_3$ requires N, 6·9; S, 23·5%). The magenta solution in ethanol had $\lambda_{max.}$ 560 mμ and changed to blue on addition of triethylamine.

In a similar preparation, involving 4-ethoxymethylene-2-ethylthiothiazol-5-one (2·17 g.) at room temperature, a magenta colour developed, but soon became degraded, and only a yellow *dye*, possibly (IV; R = $CS_2Et$), was isolated. It recrystallized from pyridine–methanol as buff needles (1·8 g.), m. p. 172° (decomp.) (Found: N, 7·9; S, 27·6%). It had $\lambda_{max.}$ 470 mμ in MeOH, and was stable to acid and alkali.

A similar *dye*, possibly (IV; R = COPh), was obtained from the reaction between the hydroxymethyl quaternary salt and 4-ethoxymethylene-2-phenyloxazol-5-one (2·17 g.) with triethylamine in ethanol. It recrystallized from nitrobenzene–ethanol as orange leaflets (1·0 g.), m. p. 289°, $\lambda_{max.}$ 467 mμ in MeOH (Found: N, 8·0; S, 9·2%).

5-[2-*Acetoxy*-2-(3-*methylbenzothiazolin*-2-*ylidene*)*ethylidene*]-3-*allyl*-2-*thiothiazolid*-4-*one*.—3-Allyl-5-[2-hydroxy-2-(3-methylbenzothiazolin-2-ylidene)-ethylidene]-2-thiothiazolid-4-one (0·5 g.) in acetic anhydride (10 c.c.) was refluxed for 10 min. The initial blue colour faded to magenta in a few minutes. The solution was cooled and poured into water (50 c.c.). The *dye* was filtered off and recrystallized from benzene–light petroleum as blue prisms, m. p. 187° (Found: N, 6·8; S, 23·9. $C_{18}H_{16}O_3N_2S_3$ requires N, 6·9; S, 23·8%). In ethanol the dye had $\lambda_{max.}$ 530 mμ, and on addition of a drop of alkali the solution became blue, and then colourless.

5-[2-*Acetoxy*-2-(3-*methylbenzothiazolin*-2-*ylidene*)-*ethylidene*]-3-*ethoxycarbonylmethyl*-2-*thiothi*-

*azolid*-4-*one*.—In the same way 3-ethoxycarbonylmethyl-5-[2-hydroxy-2-(3-methylbenzothiazoline-2-ylidene)-ethylidene]-2-thiothiazolid-4-one was acetylated. The *product* recrystallized from benzene–light petroleum as magenta needles, m. p. 164°, $\lambda_{max.}$ 532 m$\mu$ in EtOH (Found: N, 6·4; S, 21·3. $C_{19}H_{18}O_5N_2S_3$ requires N, 6·2; S, 21·3%).

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