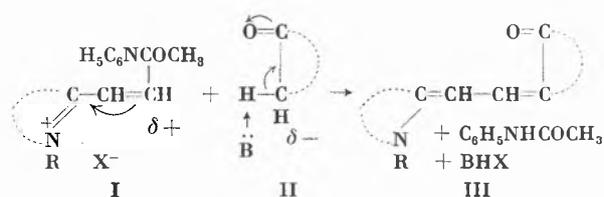


Merocyanines and Cyanines Derived from 2-Hydroxy- and 2-Mercaptothiazoles. Their Synthesis and Absorption Properties

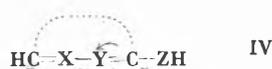
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In the photographic industry, merocyanine dyes are used extensively in order to extend the spectral sensitivity of the silver halide grains to longer wavelengths. Particularly important are the dimethinmerocyanines (III), which are usually prepared by reacting a 2-acetanilidovinyl derivative of a heterocyclic quaternary salt (I) with a keto-methylene compound (II) in the presence of a base (B). Almost without exception the dyes contain an auxochromic carbonyl group adjacent to the carbon atom carrying the chain.

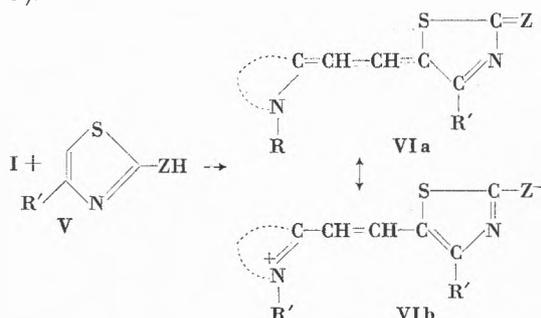


The electrophilic attack by I on II is analogous to a similar attack by the diazonium cation. In seeking the synthesis of merocyanines in which the auxochromic carbonyl group is not adjacent to the chain, attention was, therefore, turned to those compounds known to couple with diazonium salts, and particularly heterocyclic hydroxy compounds of general structure IV (X, Y:CR or N, Z:O).



In order to prevent reaction occurring at Y, this position must be blocked, i.e., Y must be nitrogen or a substituted carbon atom.

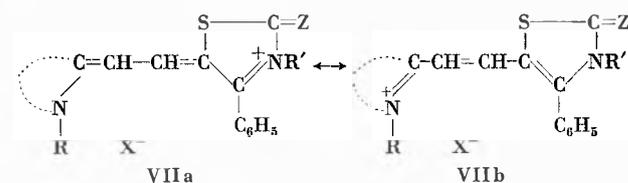
This paper will describe experiments with thiazoles, which fall under the general formula IV. It is known¹ that 2-hydroxy-4-phenylthiazole (V; R':C₆H₅, Z:O) will couple with diazonium salts in the 5-position; it also couples with I to give stable dyes (VIa; R':C₆H₅, Z:O).



¹ GANAPATHI and VENKATARAMAN, *Proc. Ind. Acad. Sci.* 22A (1945) 345.

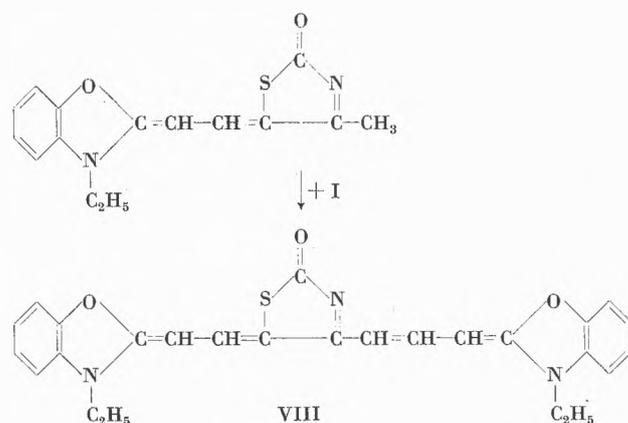
Similarly 2-mercapto-4-phenylthiazole (V; R':C₆H₅, Z:S) gave the related, more deeply coloured dye (VIa; Z:S).

All these dyes, in which the left-hand nucleus was 3-alkylbenzoxazoline, 3-alkylbenzothiazoline, 3-alkylthiazolidine and 1-alkyldihydroquinoline, were easily quaternized by alkyl esters to give true cyanines (VIIa ↔ VIIb) which absorb at considerably shorter wavelengths than the parent merocyanine bases.



The condensation of 2-(2'-acetanilidovinyl)-3-ethylbenzoxazolium iodide with 2-hydroxy-4-methylthiazole (V; R:CH₃, Z:O) in the presence of alcoholic sodium ethoxide and pyridine gave, initially, a yellow solution, the expected colour by analogy with the 4-phenyl analogue. This colour was, however, rapidly degraded on further heating and replaced by an intense, blue-green coloration. The dye which was isolated gave blue solutions in pyridine. Analogous dyes were obtained from benzothiazolium and 1,3,3-trimethylindoleninium salts.

Since the only structural change was the replacement of the 4-phenyl by the 4-methyl group in the thiazole ring, it was presumed that this latter group, when present in the initially formed, yellow, normal dye, became nucleophilic and condensed with a second molecule of 2-(2'-acetanilidovinyl)-3-ethylbenzoxazolium iodide to give the trinuclear dye VIII.

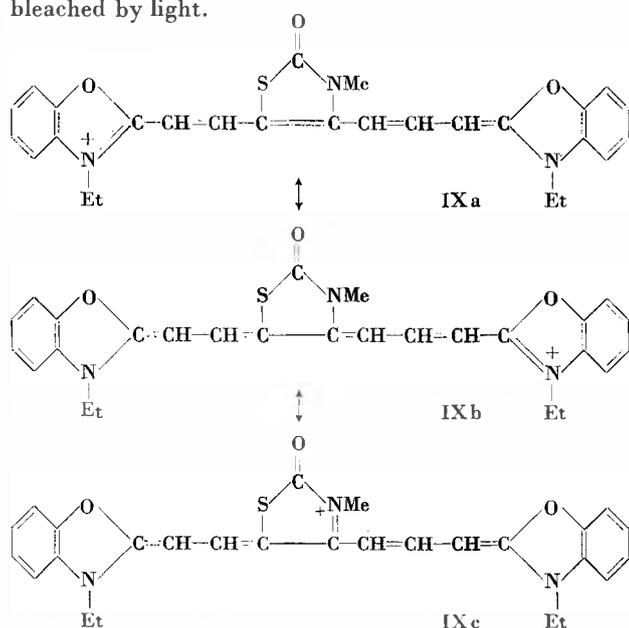


Analysis of VIII and analogues confirmed this, but in each case, one molecule of ethanol was tenaciously held. Treatment of VIII with methyl iodide gave the true

Table 1: Absorption of Merocyanines VI and VIII

Dye	X	Pyridine		Pyridine and Water (1:1)		Pyridine and Water (1:3)		Total Shift (λ)	Isoenergetic λ_{max} calculated ($m\mu$)	Deviation	
		$\lambda_{max} m\mu$	$\epsilon_{max} \times 10^{-4}$	$\lambda_{max} m\mu$	$\epsilon_{max} \times 10^{-4}$	$\lambda_{max} m\mu$	$\epsilon_{max} \times 10^{-4}$			Pyridine	Pyridine and Water (1:3)
3-Methylthiazolin-2-	O	504	8.7	492	5.4	485	5.0	-19	492	-12	+7
	S	580	5.2	535	4.3	500	2.6	-80			
3-Ethylbenzoxazolin-2-	O	518	8.5	513	6.25	507	5.7	-11	512	-6	+5
	S	596	4.35	550	2.85	516	?	-80			
		522	2.4	530	2.7						
3-Ethylbenzothiazolin-2-	O	553	9.4	547	7.95	542	7.05	-11	547	-6	+5
	S	634	8.5	580	4.85	560	4.2	-74			
1-Ethyl-1,2-dihydroquinolin-2-	O	592	7.95	560	6.6	550	6.05	-42	571	-21	+21
		564i									
	S	655i	4.55	616	4.8	607	5.1	-48?			
		621	6.9	567	3.6	563	4.1				
		577i	2.6								
1-Ethyl-1,4-dihydroquinolin-4-	O	653	8.1	595	5.5	580	4.5	-73	622	-31	+42
		608i									
3-Ethylbenzoxazolin-2-		625	8.1	657	8.8	661	10.0	+36			
		465	3.0	459	3.2	457	3.3				
3-Ethylbenzothiazolin-2-		684	8.9	715	9.7	725	10.0	+41			
		499	3.65	494	3.1	497	2.9				
1,3,3-Trimethylindolenin-2-		640	5.9	680	7.25	685	8.5	+45			
		492	2.5	492	2.9	492	2.75				

cyanine IX a \leftrightarrow IX b, solutions of which are easily bleached by light.



Analogous experiments with I and 4-methylthiazole-2-thiol gave intensely and deeply coloured solutions which degraded rapidly. In one experiment, 2-(2'-acetanilido-vinyl)-3-ethylbenzoxazolium iodide and 4-methylthiazole-2-thiol in pyridine with triethylamine gave an intensely purple solution fading to orange and yielding 3,3'-diethyl-oxacarbocyanine iodide in low yield. The cyanine IX is a higher vinylogue of dyes obtained by Nys² by a different method.

The Absorption of the Dyes

a) Merocyanines (VI)

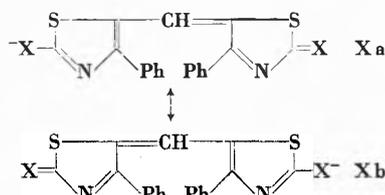
A consideration of the two extreme resonance structures of these dyes (VIa, VIb) shows that, whereas in the classical structure VIa both heterocycles are non-aromatic, in the dipolar structure both rings—in the benzazole and quinoline series—are now stabilized by aromatic resonance. Consequently, it would be expected that VI would be strongly polar. It would also be ex-

² Nys, Brit. Pat. 789077.

pected that VI (X:S) would be more strongly polar than VI (X:O) by virtue of the stronger +M effect of the C=S group. Both these expectations were confirmed by the solvatochromic behaviour of the dyes (Table 1). They all show hypsochromic shifts with increasing solvent polarity. These shifts are particularly pronounced in the thione dyes which is an indication³ of their higher degree of polarity. This is also indicated by the lower extinction coefficients of the sulphur dyes, compared with the oxygen analogues.

It is of interest to note that for VI (X:O) the strongly basic 1-ethyl-1,2-(or 1,4)-dihydroquinolinylidene dyes give a much greater total shift than the less basic nuclei. This would be expected as a result of their greater polarity. In the series VI (X:S) the same pattern is not observed. In this case the dihydroquinoline dye shows a more complex spectrum but the maximum shift is smaller than in the case of the other dyes which show a constant shift. The reason for this is not known.

In order to determine the degree of energetic asymmetry of these dyes by BROOKER's deviation method⁴ it was necessary to obtain the absorption peak of the oxonol, the anion of which is X(X:O or S). Since the merocyanines VI are the structural hybrids of X and the



appropriate trimethincyanine, the calculated absorption peak of VI at the iso-energetic point is the mean of the peaks of X and the trimethincyanine. Any deviation from this value to the shorter wavelength side is a measure of the loss of energetic symmetry of the hybrid. Using fairly drastic conditions of synthesis the oxonol X(X:O) was obtained. The Table shows the deviations given by the merocyanines VI. It will be noted that in pyridine VI (X:O) shows negative deviations in all cases, being greatest for the strongly basic nuclei. In 50% aqueous pyridine the first three dyes show no deviation, whilst the quinolines show positive deviations. In pyridine-water (1:3) all show positive deviations.

The reason for this unusual negative deviation is not known, but it may be a steric effect in the oxonol, a model of which shows that the phenyl groups are not co-planar with the rest of the molecule. A consequence of this would be a hypsochromic shift of the oxonol peak.

Since all the absorption peaks of the dyes VI (X:S) lie to longer wavelengths than the calculated isoenergetic peak for VI (X:O) it is clear that the replacement of X:O by X:S has a profound bathochromic effect on absorption. Similar shifts have been noted in other mero-

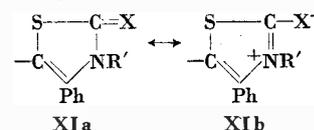
³ BROOKER, KEYES and HESELTINE, *J. Amer. Chem. Soc.* 73 (1951) 5350.

⁴ BROOKER *et al.*, *ibid.* 67 (1945) 1881, 73 (1951) 5332.

cyanines by NYS⁵ and in cyanines by WIZINGER.⁶ It is believed to be a function of the greater free energy change involved in the process $C=S \rightarrow C^+ - S^-$ compared with that of $C=O \rightarrow C^+ - O^-$, i.e., the stronger +M effect of the C=S group compared with the C=O group. In terms of the energy picture of extreme and excited structures, it means that there is a greater energy jump as the electron leaves the negatively charged sulphur atom in the dipolar extreme structure VIb, to give an excited structure, compared with the energy change as it leaves the analogous oxygen atom. It is entirely analogous to the deeper absorption of cyanines or merocyanines containing strongly basic (-M) nuclei e.g. 1-alkyldihydropyridines or quinolines^{7a}. The bathochromic effect of increasing such energy differences are forecast by the "steeper and deeper" rule of BROOKER and SKLAR^{7b} (see also KNOTT)^{7c}.

b) Cyanines (VII)

These dyes are interesting in that they all show much shorter wavelengths absorption than the parent merocyanines. This hypsochromic effect of quaternization is clearly a result of an increase in the energetic asymmetry of the hybrid. In structure VIIa neither ring has aromatic stabilization. In addition the adjacency of the positively charged nitrogen atom to the electrophilic C=X carbon atom will result in a high energy structure. In VIIb, aromatic resonance in the left-hand nucleus is present, whilst the right-hand nucleus is stabilized by amide resonance (XIa \leftrightarrow XIb) and aromatic resonance in XIb. An energetically, highly asymmetric



hybrid would, therefore, be expected.

c) Trinuclear Merocyanines (VIII) and Cyanines (IX)

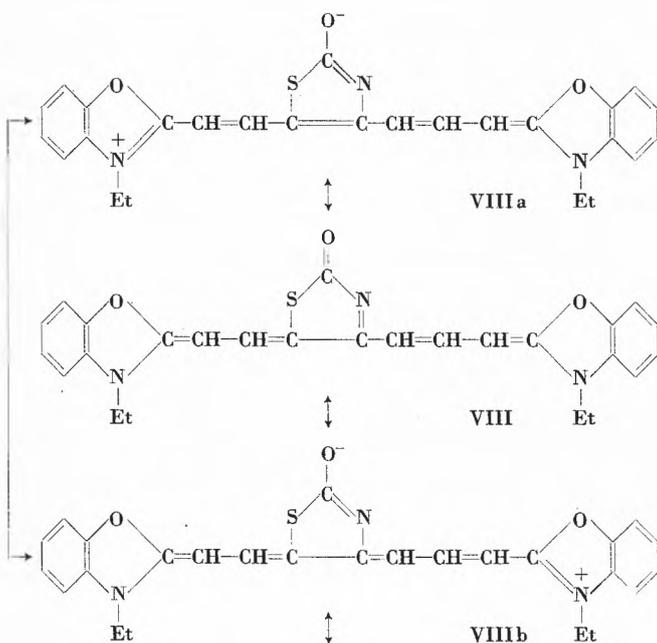
These merocyanines (VIII) contain a crossed conjugation system with the major extreme structures VIII, VIIIa and VIIIb. The resonance systems consist of two merocyanine types (VIII \leftrightarrow VIIIa and VIII \leftrightarrow VIIIb) and a cyanine type VIIIa \leftrightarrow VIIIb. The system VIII \leftrightarrow VIIIa is the same as is present in the simple merocyanine VIa \leftrightarrow VIb (X:O), which, as has been shown, is one of low asymmetry. On the other hand, the system VIII \leftrightarrow VIIIb will be of considerably higher

⁵ NYS, *Compte Rendu du 27^e Congrès international de Chimie industriel (Bruxelles 1954)*, *Ind. Chim. Belge* 20 (1955) 3, Special No. 635.

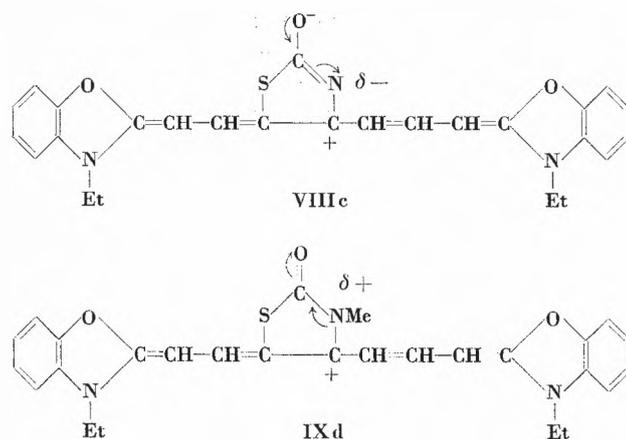
⁶ WIZINGER, *ibid.* Special No. 20, with ULRICH, *Helv. Chim. Acta* 39 (1956) 207, 217.

⁷ a) BROOKER, WHITE and SPRAGUE, *J. Amer. Chem. Soc.* 73 (1951) 1087. - b) BROOKER and SKLAR, *Rev. Mod. Physics* 14 (1942) 275. - c) KNOTT, *J. Chem. Soc.* 1951, 1024.

asymmetry since, unlike in VIIIa, the dipolar extreme structure is not stabilized by aromatic resonance in the central ring. The short wavelength peak of VIII can, therefore, be ascribed to the transition VIII \leftrightarrow VIIIa modified by VIII \leftrightarrow VIIIb. The effect of the modifica-



tion will be to shift this peak hypsochromically from that of the related simple merocyanine VI. This effect is depicted in VIIIc, an important excited structure of the hybrid. The effect of replacing a 4-phenyl group by the



3-ethylbenzoxazolin-2-ylideneprop-1-enyl group, which has a strong -M effect, is to stabilize VIIIc and cause a hypsochromic shift.^{7c}

The relatively low sensitivity of the position of this second peak to change in solvent polarity (Table 1) compared with that of VI may well be a function of the opposition by the system VIII \leftrightarrow VIIIb to electron movement into the central ring by the main system VIII \leftrightarrow VIIIa.

The long wavelength band of VIII must be ascribed to the system VIIIa \leftrightarrow VIIIb. This is a non-degenerate system, structure VIIIa being, for reasons given above, of lower energy than VIIIb. It is perhaps, unexpected that with a charge-transfer system this long wavelength peak associated with it is sensitive to solvent environment, a bathochromic shift occurring with increasing solvent polarity. It may be a result of a decrease in non-degeneracy, by the increasing solvent polarity stabilizing structure VIIIb more than VIIIa.

That VIIIa \leftrightarrow VIIIb does represent the hybrid responsible for the long wavelength peak is indicated by a comparison of the spectra in methanol of VIII (λ_{max} 643, 454 m μ) with its quaternized product, the cyanide IX (λ_{max} 695, 433 m μ). The two peaks of VIII also appear in IX, the longer wavelength peak of VIII being shifted bathochromically, the shorter wavelength peak being shifted hypsochromically, on quaternization. Both these shifts were expected^{7c} for the following reasons.

As indicated for the quaternized merocyanines VII, the effect of quaternization is to impart a high degree of energetic asymmetry to the system IXa \leftrightarrow IXc. As in the case of VII compared with the parent VI so also in the case of IX compared with VIII a shorter wavelength absorption of the short wavelength peak should be given.

In comparing the resonance systems VIIIa \leftrightarrow VIIIb with IXa \leftrightarrow IXb the only structural difference is in the central ring, the group attached to the central carbon atom of the chain. The most significant structure in each case in which this chain carbon atom is charged is VIIIc and IXd respectively. In the case of VIIIc this structure is stabilized by the electron shifts shown by the curved arrows. Such shifts will, therefore, give a hypsochromic shift.⁷ On the other hand the related shifts in IXd will make this structure less stable and thus function bathochromically.⁷ The long wavelength peak of IX would, therefore, be expected to be at longer wavelength than that of VIII.