904. *The Colour of Organic Compounds. Part VI.* A Comparison of Isomeric Dyes from 3-Alkyl-2-thiothiazolid-4- and -5-ones.*

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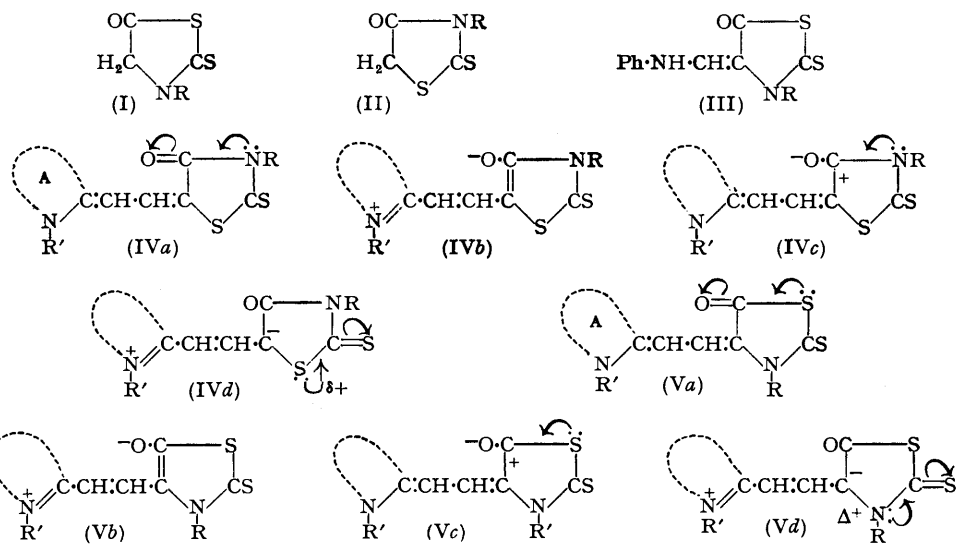
*mero*Cyanines derived from 3-alkyl-2-thiothiazolid-5-ones have been prepared.† Their absorption peaks in methanol lie at longer wave-lengths than those of the isomeric dyes from 3-alkyl-2-thiothiazolid-4-ones. It is shown that this difference is largely a function of the lower degree of energetic asymmetry of the former dyes but that the former nucleus has also the higher intrinsic colour value.

COOK and COX (*J.*, 1949, 2338) have reported the preparation of 3-alkyl-2-thiothiazolid-5-ones (I; R = Me, Pr^i) and have shown that these compounds contain a reactive nucleophilic $C_{(4)}$ in that they readily condense with benzaldehyde. The compounds are isomeric with the 3-alkylrhodanines (3-alkyl-2-thiothiazolid-4-ones) (II) and it was of interest to determine the effect of this isomerism on the colour of the derived *mero*cyanines.

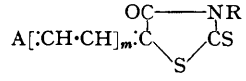
Preparation of (I; R = Me, Et, or *cyclo*hexyl) was carried out according to Cook and Cox's procedure (*loc. cit.*), but (I; R = *n*-heptyl) was obtained in better yield by treating

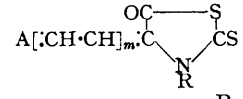


the condensation product of *N*-*n*-heptylglycine amide and carbon disulphide with phosphorus trichloride instead of hydrochloric acid.

* Part V, *J.*, 1951, 3038. † Some of these intermediates and dyes have been prepared independently, and patented, by Doyle (B.P. 662,776) and Doyle, Lawrence, and Kendall (B.P. 662,775).

TABLE 1. *Variation of dye absorption maxima (mμ) with 3-substituents in the thiazolid-4(and -5)-one ring and with solvent polarity.*

(IV) 

(V) 

A		R = Me; MeOH	R = *n*-heptyl; MeOH	R = *cyclo*hexyl; MeOH	R = Et: Benzene	R = Et: MeOH	R = Et: Aq. MeOH (1 : 2)	Calc. (degenerate)
	m = 0.							
3-Methylbenzothiazolin-2-ylidene	IV [d]	—	—	—	429	427	423	—
	V	440	—	—	441	411	439	—
	m = 1.							
1 : 3 : 3-Trimethylindolin-2-ylidene	IV [d]	—	—	—	490	505	515	537
	V	517	—	—	502 (516i) [f]	(500i) 518 [f]	(506i) 530 [f]	—
3-Methylthiazolidin-2-ylidene	IV	—	485	—	(457i) 471	484 [c]	489	487
	V	484	494	492	473, 489	492	492	—
3-Ethylthiazolidin-2-ylidene	IV	—	—	—	(459i) 472	483 [b]	491	488 (448·5)
	V	495	—	494	475 (489)	494	496	—
3-Ethylbenzoxazolin-2-ylidene	IV	—	495	—	483	490 [b]	510	508 (507·5)
	V	505	509	509	489 (506)	510	(494) 515	—
3-Ethylbenzothiazolin-2-ylidene	IV	—	—	—	513	526 [b]	533	545 (545)
	V	541	548	548	537	545	549	—
3-Ethylbenzoselenazolin-2-ylidene	IV	—	—	—	515	528 [b]	542	551 (551)
	V	540	546	548	541	546	552	—
3-Ethylnaphtho(1′ : 2′-4 : 5)thiazolin-2-ylidene	IV	—	—	—	532	545 [b]	554	564 (563·5)
	V	—	564	—	556	564	568	—
1-Ethyldihydroquinolin-2-ylidene	IV	—	—	—	538 (565i)	(535) 655 [b]	(543) 572 [a]	568 (568)
	V	561 (584)	—	563 (585)	(543) 573	562 (585)	568 (—)	—
1-Ethyldihydroquinolin-4-ylidene	IV	—	—	—	569 (604)	(577) 614 [b]	(569i) 605	618 (618·5)
	V	—	—	—	598 (639)	(604) 643	(—) 632	—
3-Ethyl-4 : 5-diphenyloxazolin-2-ylidene	IV	—	—	—	508	514	519	519
	V	—	—	—	(503i) 529 [g]	522 [g]	519 [g]	—
3-Ethyl-4 : 5-di-2′-naphthyloxazolin-2-ylidene	IV	—	—	—	515	521	526	—
	V	—	—	—	536	530	527	—
3-Ethyl-4 : 5-diphenylthiazolin-2-ylidene	IV	—	—	—	546	550	563	560
	V	—	—	—	(544i) 573 [g]	569 [g]	558 [g]	—
	m = 2.							
3-Ethylbenzoxazolin-2-ylidene	IV	—	—	—	550	580 [b]	595 [a]	596 (596·5)
	V	—	—	—	577 [e]	597 [e]	612 [e]	—
3-Ethylbenzothiazolin-2-ylidene	IV	—	—	—	573	607 [b]	624	631 (631·5)
	V	—	—	—	580	642	646	—

Figures in parentheses denote minor peaks, " i " indicating an inflection.

Values of $\lambda_{max.}$ (calc.) in parentheses are those obtained by Brooker *et al.*, *J. Amer. Chem. Soc.*, 1951, **73**, 5332.

[a] Insufficiently soluble in 1 : 2 aqueous methanol. A solvent mixture of 1 : 1 : 1 water–methanol–pyridine was used. [b] These values closely agree with values given by Brooker *et al.* (*loc. cit.*). [c] The same value is given by Hamer and Rathbone, *J.*, 1943, 248. [d] Prepared according to Fry and Kendall, B.P. 489,335/1938. [e] The thiazolid-5-one ring carries a 3-methyl substituent. [f] The thiazolid-5-one ring carries a 3-*n*-heptyl substituent. [g] The thiazolid-5-one ring carries a 3-*cyclo*hexyl substituent.

The 3-alkyl-2-thiothiazolid-5-ones are less stable than the corresponding 4-ketones and decompose when kept or during attempted recrystallization. They were therefore converted into dyes without prior purification. They form stable 4-anilinomethin derivatives (III) with *N*-ethyl*iso*formanilide (cf. Knott, U.S.P. 2,515,878). The *mero*cyanines were obtained from (I) by standard methods. Some of the related dyes from (II) are known, and their absorptions in certain solvents have been recorded by Brooker, Keyes, Sprague, van Dyke, van Lare, van Zandt, White, Cressman, and Dent (*J. Amer. Chem. Soc.*, 1951, **73**, 5332).

Table 1 gives the absorption maxima of the *mero*cyanines (IV) and (V) derived from (II) and (I) respectively. It will be observed that the nature of R is without effect on $\lambda_{max.}$ except where R = Me. As noted by Brooker and White (*ibid.*, 1935, **57**, 2480) in the cyanine series the *N*-methyl dyes are perceptibly lighter than the rest of the series with $\lambda_{max.}$, in the present case, lying up to 8 mμ to shorter wave-lengths.

It is also evident that, in methanol, dyes (V) are always deeper than (IV). The reason may, *a priori*, be twofold. It may be a result (i) of the resonance system in (V), which is responsible for visible absorption, more closely approaching degeneracy than the analogous system in (IV) or (ii) of the higher intrinsic colour value * of nucleus (I) compared with that of (II). The separation of these two factors is not difficult.

(i) Brooker *et al.* (*loc. cit.*) have shown that *mero*cyanines like many other dyes, contain resonance systems which may be divided into three types depending on the natures of the end nuclei. The system may be non-degenerate owing to the energy of the classical extreme structure being (*a*) lower or (*b*) higher than that of the dipolar extreme structure; or (*c*) the system may be near or accidentally degenerate owing to the approximate equivalence in energy of the two extreme structures. Dyes of type (*a*) contain a basic heterocyclic nucleus (A in IV, V) with a low $-M$ effect or a ketonic nucleus of low $+M$ effect. The transition from (*a*) through (*c*) to (*b*) can then occur by increasing the $+M$ or $-M$ effect of either nucleus. The polarization of the dye molecule can also be increased by increasing the polarity of the solvent.

It is well known that, for closely related dyes in which other factors are neglected, the loss of non-degeneracy is always associated with a bathochromic shift (Förster, *Z. Elektrochem.*, 1939, **45**, 548; Schwarzenbach, *ibid.*, 1941, **47**, 40; Brooker and Sprague, *J. Amer. Chem. Soc.*, 1941, **63**, 3703). Consequently it is found that dyes of type (*a*) show appreciable bathochromic shifts as solvent polarity is increased, those of type (*c*) being much less susceptible to solvent polarity changes; dyes of type (*b*) show hypsochromic shifts with increased solvent polarity. All the dyes of type (IV) examined by Brooker *et al.* (*loc. cit.*) belong to class (*a*), so that if (i) is correct then it follows that the $+M$ effect of (I) is greater than that of (II). This would be expected from the following resonance consideration.

The relative $+M$ effects of (I) and (II) are dependent on the change in energies of these nuclei on proceeding from (V*a*) to (V*b*) and from (IV*a*) to (IV*b*) respectively. In order that (IV*b*) or (V*b*) can contribute it is necessary that the intranuclear resonance denoted by the curved arrows in (IV*a*) and (V*a*) should be excluded. Such exclusion will increase the energy of the nucleus to an extent determined by the degeneracy of this intranuclear resonance system. Since the $-M$ effect of nitrogen is much greater than that of sulphur the energy associated with the amide resonance in (IV) would be higher than that of the thiocarboxylate resonance in (V), and the $-M$ effect of (I) would consequently be higher than that of (II). The same conclusion is reached if it is considered that the $+M$ effect of the carbonyl group is more highly neutralized by intranuclear resonance in (II) than in (I). The electronic influence of the rest of the ketonic nucleus on its $-M$ effect may justifiably be left out of the consideration.

The absorption figures (Table 1) of these dyes in different solvents confirm the correctness of the above view. In this table the nuclei A are given in the order of increasing $-M$ effect (cf. Brooker, *Rev. Mod. Phys.*, 1942, **14**, 275; Knott and Williams, *J.*, 1951, 1586). All the dyes down to those derived from 3-ethylnaphtho(1′ : 2′-4 : 5)thiazoline

* The intrinsic colour values of two nuclei can only be compared in a degenerate resonance system.

show a bathochromic shift of $\lambda_{max.}$ with increasing solvent polarity, the shift being much larger for (IV) than for (V) and thus indicating the higher energetic asymmetry of the former. Neglecting the quinoline dyes which are anomalous and proceeding down the table to 3-ethyl-4 : 5-diphenylthiazoline show that whereas dyes (IV) have still not achieved degeneracy the related dyes (V) have passed beyond the point of degeneracy and all show hypsochromic shifts on increased solvent polarity.

These measurements thus clearly show that differences in the degree of degeneracy of the dye pairs at least partly account for their difference in absorption.

(ii) That there is also a difference in the intrinsic colour value of the nuclei (I) and (II) can be shown in two ways. (*a*) Experimentally, the degenerate value of $\lambda_{max.}$ of (IV) has not been obtained but the calculated value is found as the mean of $\lambda_{max.}$ of the related symmetrical oxonol and carbocyanine (Table 1). This shows that the lower members of series (IV) in Table 1 are near-degenerate in aqueous methanol and it also shows that this theoretical degenerate value of (IV) still falls short of the maximum experimental values of (V). Unfortunately it is not possible to determine the calculated degenerate values of (V) because the monomethinoxonol could not be synthesized. Even if it were available, however, its $\lambda_{max.}$ would be of little value, as the molecule, unlike the oxonol of (II), is crowded and cannot be planar. If the calculated mean of $\lambda_{max.}$ of the symmetrical cyanines and less crowded trimethinoxonols is taken as the degenerate values of (IV) and (V), then a value is obtained which is much lower than that obtained by the other method and leads to positive deviations instead of the usual negative values. (*b*) True, experimentally determined values of $\lambda_{max.}$ of the degenerate trimethinoxonol anions of these nuclei show that a shift from 613 (Brooker *et al.*, *loc. cit.*) to 633 mμ occurs on replacement of (II) by (I). The difference in intrinsic colour values of the nuclei in this region of the spectrum is thus 10 mμ.

This difference would be predicted by the general colour rule of Part I (*J.*, 1951, 1024). To apply this rule it is necessary to consider those ionic excited structures in which the carbon atoms of the chromophore at which the structural changes take place carry either a positive or a negative charge. The more significant pairs of such structures (IV*c*)—(V*c*) and (IV*d*)—(V*d*) are then considered. It can be shown that structure (IV*c*) is more significant than (V*c*) in their respective hybrids as a result of the stronger (stabilizing) $-M$ effect of the –NR– group in (IV*c*) compared with the $-M$ effect of the –S– atom in (V*c*). It can also be shown that owing to the higher $+I$ effect of N compared with S the excited structure containing $-\overline{C}_{(4)}-$ in (IV) is also more significant than that containing $-\overline{C}_{(5)}-$ in (V), so that, although such structures are considered to be less significant than (IV*c*)—(V*c*), the above replacement of an –NR– group by –S– will function bathochromically irrespectively of the nature of the excited structures chosen.

This shift will, however, be offset by the reversed structural change at the adjacent carbon atom. Thus (IV*d*) will be less significant than (V*d*) because of the lower (stabilizing) positive charge on the heteroatom vicinal to the negatively charged carbon atom. The resultant shift on replacing –S– by –NR– will then be hypsochromic. It would be expected, however, that the bathochromic effect would predominate since this is a result of a π-electron ($-M$) stabilization whilst the hypsochromic effect is a result of σ-electron ($-I$) stabilization.

Experimental

Microanalyses are by Drs. Weiler and Strauss, Oxford. M. p.s are uncorrected.

Alkylaminoacetonitriles.—These were prepared according to the method of Cook and Cox (*J.*, 1949, 2334). The alkylamine (1·1 mols.) in methanol (50 c.c.) was added to hydroxyacetonitrile (57 g., 1 mol.) in methanol (50 c.c.), and the solution left for 1 day at room temperature. The methanol was removed at the pump, and the product distilled under a vacuum. The yields were as follows: ethylaminoacetonitrile, b. p. 41—42°/3 mm., 50%; n-*heptylaminoacetonitrile*, b. p. 112°/8 mm., 90% (Found: N, 18·0. $C_9H_{18}N_2$ requires N, 18·2%); cyclo*hexylaminoacetonitrile*, b. p. 74—76°/1 mm., m. p. 18°, 92% (Found: N, 20·0. $C_8H_{14}N_2$ requires N, 20·2%) (Zelinsky and Arzibacheff, *Ber.*, 1907, **40**, 3053, obtained the hydrochloride from *cyclo*hexylamine hydrochloride, formaldehyde, and potassium cyanide).

TABLE 2.

3-Subst.	Solvent (recryst.) [a]	Appearance (reflex)	M. p.	Formula	Found, N, %	Found, S, %	Reqd., N, %	Reqd., S, %
4-(3-*Methylbenzothiazolin*-2-*ylidene*)-2-*thiazolid*-5-*ones*.								
Me	C_6H_6–pet	Red prisms	240°	$C_{12}H_{10}ON_2S_3$	9·2	—	9·5	—
Et	EtOH	Red needles (green)	176	$C_{13}H_{12}ON_2S_3$	8·9	30·7	9·1	31·2
4-(3-*Methylthiazolidin*-2-*ylidene-ethylidene*)-2-*thiothiazolid*-5-*ones*.								
Me	EtOH	Red needles	234	$C_{10}H_{12}ON_2S_3$	10·5	—	10·3	—
Et	$CHCl_3$–pet	Deep pink	230	$C_{11}H_{14}ON_2S_3$	9·6	—	9·8	—
n-C_7H_{15}	EtOH	Red needles (green)	123	$C_{16}H_{24}ON_2S_3$	—	27·1	—	27·0
*cyclo*Hexyl	C_5H_5–pet	Maroon needles	306	$C_{15}H_{20}ON_2S_3$	8·1	28·3	8·23	28·3
4-(3-*Ethylthiazolidin*-2-*ylidene-ethylidene*)-2-*thiothiazolid*-5-*ones*.								
Me	C_6H_6–pet	Chocolate needles	216	$C_{11}H_{14}ON_2S_3$	—	33·5	—	33·6
Et	,,	Deep red prisms	194	$C_{12}H_{16}ON_2S_3$ [c]	9·2	31·8	9·3	32·0
*cyclo*Hexyl	EtOH–Et_2O	Turquoise-blue prisms	230—231	$C_{16}H_{22}ON_2S_3$	7·6	—	7·9	—
2-*Thio*-4-(1 : 3 : 3-*trimethylindolin*-2-*ylidene-ethylidene*)*thiazolid*-5-*ones*.								
Me	C_6H_6–pet	Yellow-green needles	260	$C_{17}H_{18}ON_2S_2$	8·2	19·6	8·5	19·4
n-Heptyl	EtOH	Yellow-green needles	117	$C_{23}H_{30}ON_2S_3$	—	15·5	—	15·5
4(3-*Ethylbenzoxazolin*-2-*ylidene-ethylidene*)-2-*thiothiazolid*-5-*ones*.								
Me	C_6H_6	Red needles	270—271	$C_{15}H_{14}O_2N_2S_2$ [f]	8·5	19·8	8·8	20·1
Et	C_6H_6–pet	Maroon needles	228	$C_{16}H_{16}O_2N_2S_2$	—	19·1	—	19·3
n-C_7H_{15}	EtOH	Orange-red needles	143	$C_{21}H_{26}O_2N_2S_2$	—	15·7	—	15·9
*cyclo*Hexyl	C_6H_6–pet	Garnet plates	222	$C_{20}H_{22}O_2N_2S_2$	—	16·6	—	16·6
4(3-*Ethylbenzothiazolin*-2-*ylidene-ethylidene*)-2-*thiothiazolid*-5-*ones*.								
Me	C_5H_5N	Grey needles	314	$C_{15}H_{14}ON_2S_3$	8·2	—	8·4	—
Et	$CHCl_3$–pet	Sepia leaflets	255	$C_{16}H_{16}ON_2S_3$	7·8	—	8·0	—
n-C_7H_{15}	EtOH	Gold plates	156	$C_{21}H_{26}ON_2S_3$ [g]	6·9	23·0	6·7	23·0
*cyclo*Hexyl	C_6H_6–pet	Green prisms	217	$C_{20}H_{22}ON_2S_3$	—	23·2	—	23·4
4-(3-*Ethylbenzoselenazolin*-2-*ylidene-ethylidene*)-2-*thiothiazolid*-5-*ones*.								
Me	C_5H_5N	Grey prisms	308	$C_{15}H_{14}ON_2S_2Se$	7·3	—	7·4	—
Et	C_6H_6–pet	Sepia needles	257	$C_{16}H_{16}ON_2S_2Se$	7·0	—	7·1	—
n-C_7H_{15}	EtOH	Gold plates	136	$C_{21}H_{26}ON_2S_2Se$	6·2	—	6·0	—
*cyclo*Hexyl	C_6H_6–pet	Green prisms	246	$C_{20}H_{22}ON_2S_2Se$ [h]	6·2	—	6·1	—
4-[3-*Ethylnaphtho*(1′ : 2′-4 : 5)*thiazolin*-2-*ylidene-ethylidene*]-2-*thiothiazolid*-5-*ones*.								
Et	C_5H_5N	Grey-green prisms	281	$C_{20}H_{18}ON_2S_3$	6·8	—	7·0	—
n-C_7H_{15}	C_6H_6–pet	Green-gold	210	$C_{25}H_{28}ON_2S_3$	—	20·3	—	20·5
4-(1-*Ethyldihydroquinolin*-2-*ylidene-ethylidene*)-2-*thiothiazolid*-5-*ones*.								
Me	EtOH	Green needles	272—274	$C_{17}H_{17}ON_2S_2$	8·3	—	8·5	—
Et	C_6H_6–pet	Yellow-green plates	241	$C_{18}H_{18}ON_2S_2$	8·1	—	8·2	—
*cyclo*Hexyl	C_5H_5N	Gold needles	264 [b]	$C_{22}H_{24}ON_2S_2$	7·0	16·0	7·1	16·1
4-(3-*Ethylbenzoxazolin*-2-*ylidenebut*-2′-*en*-1′-*ylidene*)-2-*thiothiazolid*-5-*one*.								
Me	C_5H_5N	Blue prisms	268	$C_{17}H_{16}O_2N_2S_2$	7·9	—	8·1	—
4-(3-*Ethylbenzothiazolin*-2-*ylidenebut*-2′-*en*-1′-*ylidene*)-2-*thiothiazolid*-5-*one*.								
Et	MeOH	Blue-grey	208	$C_{18}H_{18}ON_2S_3$	7·6	—	7·5	—
5-(3-*Ethyl*-4 : 5-*diphenyloxazolin*-2-*ylidene-ethylidene*)-2-*thiothiazolid*-4-*one*.								
Et	C_6H_6–pet	Red needles (blue)	231	$C_{24}H_{22}O_2N_2S_2$	—	14·6	—	14·7
4-(3-*Ethyl*-4 : 5-*diphenyloxazolin*-2-*ylidene-ethylidene*)-2-*thiothiazolid*-5-*one*.								
*cyclo*Hexyl	,,	Red-bronze leaflets	286	$C_{28}H_{28}O_2N_2S_2$	—	12·9	—	13·1
5-(3-*Ethyl*-4 : 5-*di*-2′-*naphthyloxazolin*-2-*ylidene-ethylidene*)-2-*thiothiazolid*-4-*one*.								
Et	,,	Red needles	225 [c]	$C_{32}H_{26}O_2N_2S_2$	5·2	—	5·2	—
4-(3-*Ethyl*-4 : 5-*di*-2′-*naphthyloxazolin*-2-*ylidene-ethylidene*)-2-*thiothiazolid*-5-*one*.								
Et	,,	Chocolate-brown	247 [d]	$C_{32}H_{26}O_2N_2S_2$	5·3	12·1	5·2	12·0
4-(3-*Ethyl*-4 : 5-*diphenylthiazolin*-2-*ylidene-ethylidene*)-2-*thiothiazolid*-5-*one*.								
*cyclo*Hexyl	,,	Green needles	240	$C_{28}H_{28}ON_2S_3$	5·7	18·8	5·5	19·0

[a] Pet. = light petroleum (b. p. 60—80°). [b] With decomp. [c] Shrinks at 156°. [d] Shrinks at 235°. [e] Found: C, 47·9; H, 5·0. Reqd.: C, 48·1; H, 5·3%. [f] Found: C, 56·5; H, 4·4. Reqd.: C, 56·7; H, 4·4%. [g] Found: C, 60·1; H, 6·0. Reqd.: C, 60·3; H, 6·2%. [h] Found: C, 53·1; H, 4·9. Reqd.: C, 52·4; H, 4·8%.

Reactions with Alkylaminoacetonitriles (cf. Cook and Cox, *loc. cit.*).—(*a*) The alkylaminoacetonitrile (1 mol.) in methanol (150 c.c.) was cooled in ice and stirred under an atmosphere of nitrogen. Carbon disulphide (76 g., 1 mol.) in methanol (150 c.c.) was slowly added, and the solution left for ½ hour. It was then poured into 4N-hydrochloric acid (1 l.) and shaken vigorously for 5 minutes. The 3-alkyl-2-thiothiazolid-5-one separated and was left for several hours before being filtered off, washed with water, and dried *in vacuo*. The yields were: 3-ethyl-2-thiothiazolid-5-one, yellow solid, m. p. 63°, 60%; 3-*n*-heptyl-2-thiothiazolid-5-one, pale yellow waxy solid, indefinite m. p., 40%; 3-*cyclo*hexyl-2-thiothiazolid-5-one, buff needles, m. p. 114°, 50%. (These compounds decomposed before analyses could be carried out.)

(*b*) n-*Heptylaminoacetamide*. *n*-Heptylaminoacetonitrile (47 g.) was dropped into ice-cold alcoholic sulphuric acid (8·1 ml. of sulphuric acid in 70 ml. of ethanol) with stirring. The nitrile hydrogen sulphate separated as white needles (50 g.), m. p. 134—135° (from ethanol). This was added slowly to sulphuric acid (130 ml.) and heated for 1 hour on the steam-bath. The liquid was cooled and dropped into ethanol (800 ml.) at 0°. n-*Heptylaminoacetamide hydrogen sulphate* separated as a white solid (61·5 g.) and crystallized from ethanol as colourless needles, m. p. 163° (Found: S, 11·9. $C_9H_{20}ON_2,H_2SO_4$ requires S, 11·85%). The amide salt was ground and suspended in methanol, and sodium methoxide was added to neutrality to phenolphthalein. The solution was then filtered and evaporated at the pump. n-*Heptylglycine amide* solidified and crystallized from ligroin as glossy plates, m. p. 62° (30 g.) (Found: N, 16·1. $C_9H_{20}ON_2$ requires N, 16·3%).

Product from n-*Heptylaminoacetamide and Carbon Disulphide*.—*n*-Heptylaminoacetamide (30 g.) in methanol (50 ml.) was cooled in ice, and carbon disulphide (13·5 g.) added. The product slowly precipitated as a yellow amorphous powder, m. p. 115° (27 g.). This compound decomposed on attempted recrystallization from various solvents, and was used directly to prepare solutions of 3-*n*-heptyl-2-thiothiazolid-5-one.

3-n-*Heptyl-2-thiothiazolid-5-one and Dimethin*mero*cyanine Dyes therefrom*.—Phosphorus trichloride (1·4 g.) was added to the intermediate (2·4 g.) in benzene (12 m.) and the solution heated on the steam-bath for 10 minutes, with good mixing. To the resulting gel was added ethanol (24 c.c.), triethylamine (4 c.c.), and the appropriate 2-2′-acetanilidovinyl quaternary salt of a heterocyclic base (0·01 mol.). The solution was heated for 15 minutes on the steam-bath, and then all solvents were distilled off at reduced pressure. The *dye* was extracted from the residual tar with ethanol and allowed to crystallize (see Table 2).

4-*Anilinomethylene-3-ethyl-2-thiothiazolid-5-one*.—3-Ethyl-2-thiothiazolid-5-one (0·8 g.) and ethyl*iso*formanilide (0·8 g.) were warmed for 1 minute on the steam-bath. Ethanol was boiled off, leaving a red solid which was washed with ether and recrystallized from ethanol–ether as bright brown needles (1 g.), m. p. 191° (Found: N, 10·5; S, 24·4. $C_{12}H_{12}ON_2S_2$ requires N, 10·6; S, 24·2%).

Dye Syntheses (see Table 2).—mero*Cyanines* were prepared by heating the 3-alkyl-2-thiothiazolid-5-one (0·01 mol.), 2-methylthiobenzothiazole ethotoluene-*p*-sulphonate (0·01 mol.), triethylamine (0·01 mol.), and ethanol on the steam-bath for 15 minutes. The solution was chilled and the dye filtered off and recrystallized. *Dimethin-* and *tetramethin*-mero*cyanines* were prepared by heating the 3-alkyl-2-thiothiazolid-4(or 5)-one (0·01 mol.), 2(or 4)-2′-acetanilidovinyl or 2-4′-acetanilidobutadienyl derivative of a heterocyclic quaternary salt (0·01 mol.), triethylamine (0·01 mol.), and ethanol on the steam-bath for 10—20 minutes. The solution was chilled and the dye filtered off and recrystallized.

Bis-[3-*ethyl-2-thio-4-thiazolid-5-one*]*trimethinoxonol*.—3-Ethyl-2-thiothiazolid-5-one (3·22 g.), β-ethoxyacraldehyde diethyl acetal (1·74 g.), and triethylamine (1·01 c.c.) in ethanol (20 c.c.) were refluxed for 10 minutes on the steam-bath. The green solution was made slightly acid with hydrochloric acid. The oxonol (0·8 g.) was obtained by filtering the chilled solution and washing the dark crystals with a little ice-cold ethanol. It could not be recrystallized without decomposition from any of the usual organic solvents.

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