1110. 2-2′-*Carboxyphenacylidenethiazolines and Related Cyanine Dyes.*

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2-2′-Carboxyphenacylidenethiazolines are prepared from phthalic anhydride and nucleophilic 2-methyl derivatives of quaternary thiazolium salts. Reaction sequences leading to related dyes, including cyanines and merocyanines with an *o*-carboxyphenyl substituent in the chain or with an indanone bridge, and phthalones are described.

Cyanine and merocyanine dyes with phenyl substituents in the polymethine chain are known sensitizers for photographic silver halide emulsions. The aim of this investigation was to provide similar dyes with improved solubility by incorporating carboxylic acid or ester groups in the chain phenyl substituent, and to examine the chemistry of the intermediates and dyes involved. Limited groups of such soluble dyes are known: Brooker and Sprague[1] described the preparation of symmetrical trimethinecyanines of this type, and more recently merocyanines derived from the thiazoline nucleus have been disclosed in a Du Pont patent.[2] The methods of preparation involved refluxing a 2-methyl heterocyclic quaternary salt with phthalic anhydride in pyridine to produce trimethinecyanines, and with additional reactive heterocyclic ketomethylene intermediates to produce merocyanines. No intermediates were described.

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[1] Brooker and Sprague, U.S.P. 2,226,156/1940.

[2] Du Pont de Nemours and Company, B.P. 753,174/1956.

To prepare a wider range of dyes with substituted phenyl groups it was desirable to obtain the 2-2′-carboxyphenacylidene derivatives of heterocyclic bases. 2-2′-Carboxyphenacylidene-3-ethylbenzothiazoline (II), a yellow solid soluble in aqueous sodium carbonate, was obtained in 52% yield by reaction of a 3-ethyl-2-methylbenzothiazolium salt with phthalic anhydride in ethanol, in the presence of triethylamine. In this reaction, other bases or basic solvents gave the same product in lower yield. The reaction in cold pyridine led to compound (II) contaminated with the trimethinecyanine dye (VI), but in boiling pyridine (Brooker) gave only dye (VI). The same benzothiazolium quaternary salt and phthalic anhydride fused together at 140° for eight hours gave a 27% yield of the yellow phthalone (I) together with some purple dye, probably the trimethinecyanine (VI). The phthalone was also prepared from 3-ethyl-2-ethylthiobenzothiazolium ethyl sulphate and indane-1,3-dione. The preparation of analogous 2-2′-carboxyphenacylidene derivatives with benzoxazole, quinoline, thiazoline, 5-chlorobenzothiazole, and naphtho-[1,2-*d*]thiazole nuclei was attempted but only those of the last two were isolated.

2-2′-Carboxyphenacylidene-3-ethylbenzothiazoline (II) underwent some interesting reactions. Heated alone at 160° it provided first the phthalate of the trimethinecyanine (VI) and then, on prolonged heating, the phthalone (I). The intermediate (II), when refluxed in acetic anhydride, gave the phthalone (I) in 79% yield. It was stable in basic media. 2′-Alkoxycarbonylphenacylidene derivatives (III; R = Me or Et) were prepared by esterification of compound (II) with a refluxing alcohol and hydrogen chloride. Alternatively, the ester (III; R = Et) was prepared from 3-ethyl-2-methylbenzothiazolium iodide and *o*-ethoxycarbonylbenzoyl chloride. *ortho*-Substituted acid, ester, and alkyl derivatives had similar ultraviolet absorption spectra (Table 1). There are small hypsochromic and hypochromic displacements in comparisons with 3-methyl-2-phenacylidenebenzothiazoline, because of the steric effect of the *ortho*-substituents.

When the intermediate (II) was treated with hydrogen halide in acetic anhydride, or warmed on the steam-bath with acetyl chloride or benzoyl chloride in acetic acid, yellow α-acetoxystyryl and α-benzoyloxystyryl quaternary salts (IV; R = Me or Ph) were formed. The corresponding α-methoxystyryl derivative (V) was obtained exothermally on mixing the 2′-carboxyphenacylidene intermediate with methyl sulphate. These styryl salts (IV and V) are unstable, and were generally used without purification. Compound (II) is not an intermediate in the dye reaction described by Brooker and Sprague[1] since it does not react in pyridine with heterocyclic quaternary salts possessing reactive methyl groups. However, in acetic anhydride with sodium acetate, reaction occurs and the products are trimethinecyanines (VIII; R = H), in which two methine groups of the polymethine chain form part of an indan-1-one ring. These products (VIII) are also formed by cyclization of *o*-carboxyphenyl-substituted trimethinecyanine dyes (VI) in the same medium. Correspondingly, dimethinemerocyanine dyes (VII) with an indan-1-one bridge were prepared from the intermediate (II) and a ketomethylene heterocyclic compound, or from chain *o*-carboxyphenyl-substituted dimethinemerocyanines (IX; R = H)

TABLE 1.

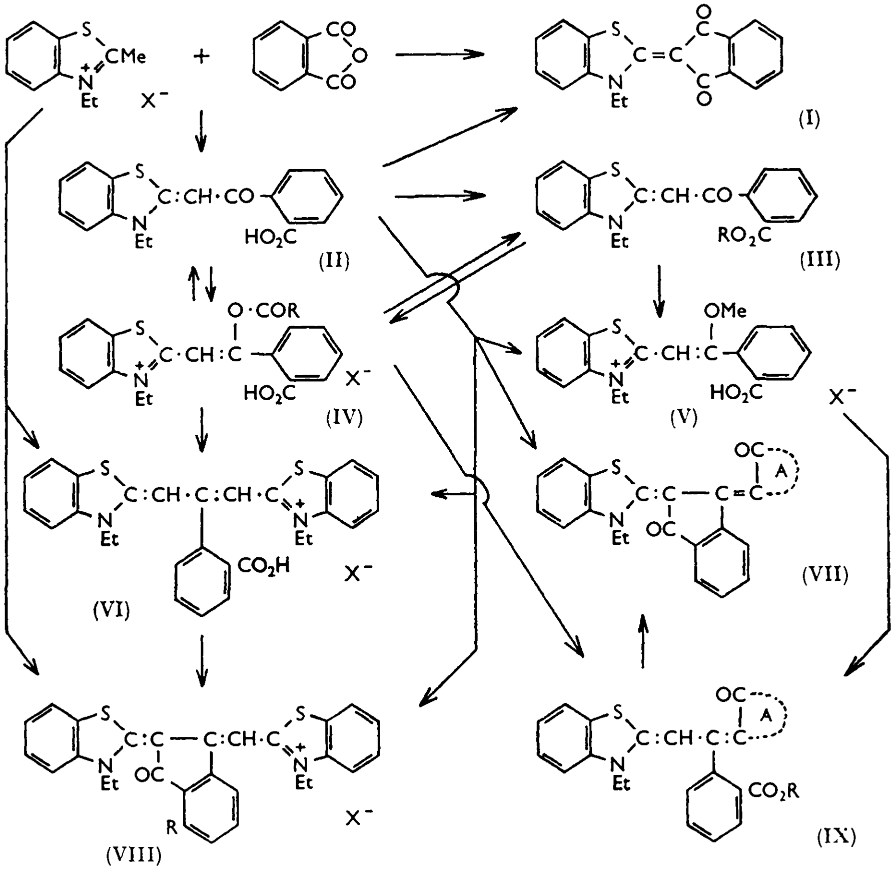
Ultraviolet absorption maxima (mμ) and extinction coefficients of 2′-substituted phenacylidenebenzothiazolines in ethanol.

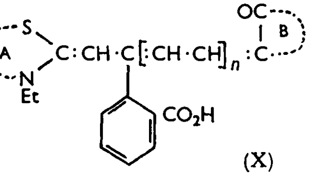
Benzothiazoline	$\lambda_{max.}$	log ε
3-Methyl-2-phenacylidene	385	4·62
3-Methyl-2-2′-methylphenacylidene	365 *	—
2-2′-Carboxyphenacylidene-3-ethyl	366	4·52
3-Ethyl-2-2′-methoxycarbonylphenacylidene	366	4·56
2-2′-Ethoxycarbonylphenacylidene-3-ethyl	366	4·58

* In MeOH (ref. 5).

(described below) in the same medium. Examples of these indanone-bridge dyes were described by Anderson [3] with little experimental detail.

In contrast with the parent carboxylic acid intermediate (II), the 2'-alkoxycarbonylphenacylidene esters (III) failed to react with nucleophilic dye intermediates in acetic anhydride and sodium acetate. Condensation of these esters with acetyl chloride in acetic acid, or fusion with methyl sulphate, gave yellow styryl salts, the properties and further reactions of which were identical with those of the α-acetoxy- and α-methoxy-2-carboxystyryl derivatives (IV and V). Hydrolysis of the esters, therefore, occurred under these conditions.

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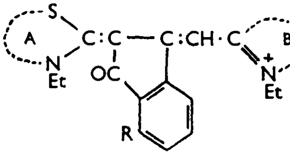
(XI)

The α-acetoxystyryl salt (IV) proved to be a highly reactive dye intermediate. In hot water, or in ethanol containing triethylamine, it gave the 2'-carboxyphenacylidene

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[3] Anderson, Scientific Photography, Proc. Internat. Colloquium, Liége, 1959, Pergamon Press, 1962, p. 487.

compound (II) or the ester (III) in high yield; in ethanol or in pyridine it gave mixtures of the 2′-ethoxycarbonylphenacylidene derivative (III) and phthalone (I), or compound (II) and the symmetrical trimethinecyanine (VI), respectively. When treated with 2-methyl heterocyclic quaternary salts or heterocyclic ketomethylene compounds in ethanol with triethylamine, it gave symmetrical and unsymmetrical trimethinecyanines such as (VI) or dimethinemerocyanines (IX; R = H), with *o*-carboxyphenyl substituents in the chain. A tetramethinemerocyanine (X; $n = 1$) was also obtained with the appropriate dye intermediate. These dyes, also preparable from α-benzoyloxystyryl or α-methoxystyryl intermediates, are soluble in aqueous sodium carbonate solution. The *o*-carboxy-substituent was readily esterified with ethanol and hydrogen chloride, as described by Brooker *et al.*,[1] to give dyes which were insoluble in aqueous carbonate and whose visible absorption spectra were virtually unchanged. The esterified dyes could not be converted into the indanone-bridged dyes (VII and VIII) by treatment with sodium acetate and acetic anhydride.

A method for the preparation of trimethinecyanines (XI) with a fused indan-1-one ring on the chain, which is not restricted to the benzothiazole family of heterocyclic ring systems, consisted of refluxing a 2-methyl heterocyclic quaternary salt with phthalic anhydride and sodium acetate in acetic anhydride.

A comparison of absorption maxima and extinction coefficients of related benzothiazoletrimethinecyanines in various solvents (Table 2) indicates that dyes substituted at the *meso*-position by phenyl and *o*-carboxyphenyl groups behave similarly. Bruylants, van Dormael, and Nys [4] and Brooker *et al.*[5] have shown that the phenyl group lies out of the

TABLE 2.

Absorption maxima (mμ) and extinction coefficients of benzothiazoletrimethinecyanine iodides in various solvents.

	In chloroform		In methanol		In water	
meso-*Substituent*	$\lambda_{max.}$	log ε	$\lambda_{max.}$	log ε	$\lambda_{max.}$	log ε
H	571	5·15	557	5·17	554	5·02
Ph	573	5·28	560	5·27	558	5·12
o-$C_6H_4{\cdot}CO_2H$ (VI; X = I)	575	5·24	561	5·27	559	5·22
[α,β-2,3]Indanone bridge (VIII; R = H, X = I)	577	4·28	570	4·23	556	—
7-Nitro-[α,β-2,3] indanone bridge (VIII; R = NO_2, X = I)	593	—	576	—	565	—

TABLE 3.

Absorption maxima (mμ) and extinction coefficients of symmetrical trimethinecyanine iodides (XI; X = I) with an [α,β-2,3]indanone bridge in various solvents.

		Solvent					
		In chloroform		In methanol		In water	
Nuclei A, B	R	$\lambda_{max.}$	log ε	$\lambda_{max.}$	log ε	$\lambda_{max.}$	log ε
Thiazoline	H	523	4·15	505	4·08	495	4·00
Thiazoline	NO_2	535	4·04	520	3·95	504	3·90
Benzoxazole	H	535	4·36	508	4·30	505	—
Benzoxazole	NO_2	544	4·08	526	4·04	519	—
2-Quinoline	H	625	4·48	595	4·30	—	—
		i590	—	—	—	i555	—
		494	4·28	493	4·28	493	—

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[4] Bruylants, van Dormael and Nys, *Bull. Cl. Sci., Acad. roy. Belg.*, 1948, **34**, 703.

[5] Brooker, White, Heseltine, Keyes, Dent, and Van Lare, *J. Phot. Sci.*, 1953, **1**, 173.

plane of the rest of the molecule, with no observable steric effect on the main planar-dye resonance system. This also applies to the *o*-carboxyphenyl group. The related indanone-bridged cyanines have absorption maxima which are weakened and moved to slightly longer wavelengths, indicating that non-planarity of the resonance system is now a significant factor. This has been noted by Anderson.[3] The introduction of a 7-nitro-group into the indanone ring system has a bathochromic effect consistent with its $+I$ action at the *meso*-carbon of the chain. The similar behaviour of other indanone-bridged cyanines is shown in Table 3.

The absorption behaviour of the merocyanines follows that of the cyanines. Both the *o*-carboxyphenyl-substituted dimethinemerocyanines and the indanone-bridged dyes absorb at longer wavelengths than the dyes unsubstituted in the chain. The indanone-bridged dyes again have low extinction coefficients and are non-planar.

EXPERIMENTAL

Absorption spectra were measured for methanol solutions. Light petroleum had b. p. 60—80°.

2-2'-Carboxyphenacylidene-3-ethylbenzothiazoline (II).—To an unheated solution of 3-ethyl-2-methylbenzothiazolium toluene-*p*-sulphonate (34·9 g., 0·1 mole) and phthalic anhydride (14·8 g., 0·1 mole) in ethanol (250 ml.), triethylamine (28·0 ml., 0·2 mole) was added. The solution was shaken for 10 min., warmed on the steam-bath for 5 min., cooled, poured into water (750 ml.), and acidified with hydrochloric acid. It was chilled overnight to yield a solid which was filtered off, washed with a little ethanol and ether, and recrystallized from ethyl acetate–ethanol–ether. The *product* (17 g., 52%), obtained as yellow leaflets, had m. p. 164° (Found: C, 66·2; H, 4·7; N, 4·2; S, 10·1. $C_{18}H_{15}NO_3S$ requires C, 66·4; H, 4·6; N, 4·3; S, 9·8%). Replacing triethylamine by sodium hydroxide, or ethanol by pyridine, in this reaction resulted in a lower yield.

The 2'-carboxyphenacylidene intermediate (II) (1·5 g.) was fused at 160° for 5 min. The melt was cooled, treated with ethanol, and recrystallized from ethanol, to give *bis-(3-ethyl-2-benzothiazole)-β-o-carboxyphenyltrimethinecyanine phthalate* (VI; X = phthalate) as green prisms (0·4 g.), m. p. 201° (decomp.) (Found: N, 4·3; S, 9·9. $C_{36}H_{30}N_2O_6S_2$ requires N, 4·3; S, 9·8%).

The intermediate (II) (5 g.) was fused at 180° for 20 min. This melt was cooled, treated with ethanol to remove the trimethinecyanine (VI; X = phthalate), and recrystallized from chloroform–ethyl acetate to give 3-ethyl-2-(1,3-dioxoindan-2-ylidene)benzothiazoline (I) identical with the product described below.

2-2'-Carboxyphenacylidene-5-chloro-3-ethylbenzothiazoline was obtained similarly as yellow leaflets, m. p. 196° (from benzene–light petroleum), in 20% yield (Found: C, 59·9; H, 4·0; N, 3·8. $C_{18}H_{14}ClNO_3S$ requires C, 60·0; H, 3·9; N, 3·9%).

2-2'-Carboxyphenacylidene-3-ethylnaphtho[1,2-d]thiazoline was obtained similarly as a green powder, m. p. 189° (from chloroform–light petroleum), in 24% yield (Found: C, 69·8; H, 4·5; N, 3·6; S, 8·7. $C_{22}H_{17}NO_3S$ requires C, 70·4; H, 4·5; N, 3·7; S, 8·5%).

3-Ethyl-2-(1,3-dioxoindan-2-ylidene)benzothiazoline (I).—(*a*) 3-Ethyl-2-methylbenzothiazolium toluene-*p*-sulphonate (17·5 g., 0·05 mole) and phthalic anhydride (7·4 g., 0·05 mole) were fused together at 140° for 8 hr. The crude *product* was treated with hot aqueous sodium carbonate, filtered off, washed with water and ethanol, and recrystallized from chloroform–ethyl acetate to give golden-yellow needles, m. p. 227° (4·0 g., 26%) (Found: C, 70·6; H, 4·3; N, 4·5; S, 10·6. $C_{18}H_{13}NO_2S$ requires C, 70·4; H, 4·2; N, 4·6; S, 10·4%), $\lambda_{max.}$ 378 mμ (log ε 4·69).

(*b*) 3-Ethyl-2-ethylthiobenzothiazolium toluene-*p*-sulphonate (2·0 g., 0·005 mole), indane-1,3-dione (0·7 g., 0·005 mole), and triethylamine (0·7 ml., 0·005 mole) in ethanol (10 ml.) were refluxed together for 10 min. From the chilled solution the product (1·1 g., 72%) was filtered off and recrystallized from chloroform–ethyl acetate as yellow needles, m. p. and mixed m. p. 227°.

(*c*) 2-2′-Carboxyphenacylidene-3-ethylbenzothiazoline (1 g.) was refluxed in acetic anhydride (10 ml.) for ½ hr. From the chilled solution the product (0·75 g., 79%) was filtered off and recrystallized from chloroform–ethyl acetate as yellow needles, identical with the above samples.

3-*Ethyl*-2-(1,3-*dioxoindan*-2-*ylidene*)*naphtho*[1,2-*d*]*thiazoline*.—2-2′-Carboxyphenacylidene-3-ethylnaphtho[1,2-*d*]thiazoline (1 g.) was refluxed in acetic anhydride (10 ml.) for ½ hr. From the chilled solution the *product* (0·65 g., 68%) was filtered off and recrystallized from pyridine–ethanol as olive-green prisms, m. p. 217° (Found: C, 73·9; H, 4·2; N, 3·8; S, 9·1. $C_{22}H_{15}NO_2S$ requires C, 74·0; H, 4·2; N, 3·9; S, 9·0%), $\lambda_{max.}$ 397 mμ (log ε 4·67).

2-2′-*Ethoxycarbonylphenacylidene*-3-*ethylbenzothiazoline* (III; R = Et).—2-2′-Carboxyphenacylidene-3-ethylbenzothiazoline (16 g.) in saturated ethanolic hydrochloric acid (500 ml.) was refluxed for 3 hr., and poured into water (3 l.). The *product* was filtered off and recrystallized from benzene–light petroleum as cream needles, m. p. 124° (7 g., 40%) (Found: N, 3·9; S, 9·0. $C_{20}H_{19}NO_3S$ requires N, 4·0; S, 9·1%).

It was identical with a sample prepared from *o*-ethoxycarbonylbenzoyl chloride and 3-ethyl-2-methylbenzothiazolium toluene-*p*-sulphonate, according to the method of Brooker and White.[6]

5-*Chloro*-2-2′-*ethoxycarbonylphenacylidene*-3-*ethylbenzothiazoline* was prepared similarly as cream needles (from benzene), m. p. 158°, in 30% yield (Found: Cl, 9·3; N, 3·6. $C_{20}H_{18}ClNO_3S$ requires Cl, 9·2; N, 3·6%).

2-(β-*Acetoxy*-2-*carboxystyryl*)-3-*ethylbenzothiazolium Bromide* (IV; R = Me; X = Br).—To a stirred suspension of 2-2′-carboxyphenacylidene-3-ethylbenzothiazoline (II) (10·0 g.) in acetic anhydride (100 ml.), a 50% solution (8 ml.) of hydrobromic acid in acetic acid was added. An exothermic reaction occurred and after ½ hr. the *product* was filtered off, washed with ether, and dried as a yellow solid (13 g., 94%). It could be rapidly recrystallized from methanol–ether as a yellow solid, m. p. 193° (decomp., darkens at 160°) (Found: Br, 18·1; S, 7·1. $C_{20}H_{18}BrNO_4S$ requires Br, 17·9; S, 7·1%). The same product, in 58% yield, was obtained by using 2-2′-ethoxycarbonylphenacylidene-3-ethylbenzothiazoline in this reaction.

2-(β-Acetoxy-2-carboxystyryl)-3-ethylnaphtho[1,2-*d*]thiazolium bromide and 2-(β-acetoxy-2-carboxystyryl)-5-chloro-3-ethylbenzothiazolium bromide were obtained analogously in 55% and 95% yield, respectively, from appropriate 2′-carboxyphenacylidene intermediates.

The corresponding chloride (IV; R = Me, X = Cl) was obtained when the 2′-carboxyphenacylidene intermediate (II) (7 g.) and acetyl chloride (20 ml.) in acetic acid (70 ml.) were heated for 1 hr. on the steam-bath. Ether (180 ml.), added to the cooled solution, precipitated the chloride (6·4 g., 79%). It was not further purified. The same product, in 45% yield, was obtained by using the ethyl ester (III; R = Et).

Replacement of acetyl chloride by benzoyl chloride in the reaction provided 2-(β-benzoyloxy-2-carboxystyryl)-3-ethylbenzothiazolium chloride (IV; R = Ph, X = Cl) in 82% yield.

2-(2-Carboxy-β-methoxystyryl)-3-ethylbenzothiazolium methyl sulphate (V; X = methyl sulphate), obtained as a yellow powder from the exothermic reaction between 2-2′-carboxyphenacylidene-3-ethylbenzothiazoline (II) and methyl sulphate, was used without purification.

Reactions of 2-(β-*Acetoxy*-2-*carboxystyryl*)-3-*ethylbenzothiazolium Salts* (IV).—2-(β-Acetoxy-2-carboxystyryl)-3-ethylbenzothiazolium bromide (1 g.) with triethylamine (1·4 ml.) in water (30 ml.) was heated on the steam-bath for ½ hr. The solution was cooled and acidified with hydrochloric acid. The product (0·6 g.) was filtered off, and recrystallized from ethyl acetate–ethanol–ether to give 2-2′-carboxyphenacylidene-3-ethylbenzothiazoline (II), m. p. 164°.

This product, contaminated with the dye (VI; X = Br), was also obtained by heating the acetoxy-salt (IV) on the steam-bath in pyridine for ½ hr.

The same acetoxy-salt (IV; R = Me, X = Br) (1·6 g.), when refluxed for 2 hr. in ethanol (100 ml.), gave compound (I) (0·4%) as the first crop. Concentration of the mother-liquor provided a second crop, identified as 2-2′-ethoxycarbonylphenacylidene-3-ethylbenzothiazoline (III; R = Et) (0·5 g.).

The acetoxy-salt (IV; R = Me, X = Cl) (1 g.) and triethylamine (1·4 ml.) were refluxed in methanol (15 ml.) for ½ hr. Water (30 ml.) precipitated the product, 3-*ethyl*-2-(2-*methoxycarbonylphenacylidene*)*benzothiazoline* (III; R = Me), which was then recrystallized from ethyl acetate as lemon-yellow needles, m. p. 182° (0·6 g., 75%) (Found: N, 4·1; S, 9·5.

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[6] Brooker and White, U.S.P. 2,112,139/1938.

$C_{19}H_{17}NO_3S$ requires N, 4·1; S, 9·4%). 2-2′-Ethoxycarbonylphenacylidene-3-ethylbenzothiazoline (III; R = Et) was obtained in 94% yield by a similar reaction in ethanol. Analogously, 2-(β-acetoxy-2-carboxystyryl)-3-ethylnaphtho[1,2-*d*]thiazolium bromide with triethylamine in ethanol gave *2-2′-ethoxycarbonylphenacylidene-3-ethylnaphtho*[1,2-d]*thiazoline* (80%) as yellow needles, m. p. 191° (from ethyl acetate–light petroleum) (Found: N, 3·4; S, 8·0. $C_{24}H_{21}NO_3S$ requires N, 3·5; S, 7·9%).

Trimethinecyanines with an [α,β-2,3]*Indanone Bridge* (XI) (*Table* 4).—(*a*) A 2-methyl-heterocyclic quaternary salt (0·02 mole), phthalic anhydride (0·01 mole) or 3-nitrophthalic anhydride (0·01 mole), and sodium acetate (2 g.) in acetic anhydride (30 ml.) were refluxed for 10 min. The solution was concentrated, then poured into water. The *dye* slowly crystallized.

TABLE 4.

Trimethinecyanine iodides with an [α,β-2,3]indanone bridge (XI; X = I).

Synthetic method (*a*) was used, except as indicated.

No.	Nuclei A, B	R	Yield (%)	M. p.	Found (%) I	Found (%) N	Found (%) S	Formula	Required (%) I	Required (%) N	Required (%) S
1	Thiazoline	H	50	228°	25·7	5·6	13·1	$C_{20}H_{23}IN_2OS_2$	25·5	5·6	12·9
2	Thiazoline	NO_2	55	256 *	23·1	7·6	12·0	$C_{20}H_{22}IN_3O_3S_2$	23·4	7·7	11·8
3	Benzoxazole	H	60	250 *	22·6	4·8		$C_{28}H_{23}IN_2O_3$	22·6	5·0	
4	Benzoxazole	NO_2	49	180	44·2	4·8		$C_{28}H_{22}I_3N_3O_5$	44·2	4·9	
5	Benzothiazole	H	66	228 *	21·8	4·5	10·8	$C_{28}H_{23}IN_2OS_2$	21·4	4·7	10·8
6	Benzothiazole	NO_2	85	183		6·7	10·6	$C_{28}H_{22}ClN_3O_7S_2$		6·9	10·5
7	2-Quinoline	H	56	202 *	22·0	4·7		$C_{32}H_{27}IN_2O$	21·8	4·8	
8	Benzothiazole, naphth-[2,1-d]oxazole	H	42	242 *	20·4	4·4	5·1	$C_{32}H_{25}IN_2O_2S$	20·2	4·5	5·1

Notes on compounds no.: (1) Sepia leaflets from MeOH–Et_2O, 46% by method (*b*). Found: C, 48·1; H, 4·7. Reqd.: C, 48·2; H, 4·6%. (2) Cryst. as (1). (3) Maroon needles from MeOH–Et_2O. (4) Maroon leaflets from $CHCl_3$–Et_2O. Found: C, 39·3; H, 2·7. Reqd.: C, 39·0; H, 2·6%. (5) Sepia prisms from MeOH–EtOAc, 72% by method (*b*), 85% by method (*c*). (6) Purple leaflets from pyridine–ethanol. *Perchlorate* gives Cl, 5·7% (Reqd., 5·8%). (7) Bronze needles from MeOH–Et_2O. (8) By method (*c*) purple needles from EtOH–Et_2O, $\lambda_{max.}$ 565 mμ (infl. 540 mμ) (log ε 4·26).

* (Decomp.)

(*b*) A β-*o*-carboxyphenyltrimethine cyanine (1 g.), of which dye (VI) is an example, in acetic anhydride (10 ml.) was refluxed for 10 min. The solution was concentrated and poured into water. The *dye* crystallized. Addition of sodium acetate (1 g.) to the reaction mixture sometimes improved the yield of dye.

(*c*) A 2-methyl-heterocyclic quaternary salt (0·01 mole), 2-2′-carboxyphenacylidene-3-ethylbenzothiazoline (0·01 mole) and sodium acetate (0·01 mole) in acetic anhydride (25 ml.) were refluxed for 10 min. The solution was concentrated and poured into water. The dye crystallized.

Merocyanines with an [α,β-2,3]*Indanone Bridge* (VII).—(*a*) 2-2′-Carboxyphenacylidene-3-ethylbenzothiazoline (II) (0·01 mole), the ketomethylene compound (0·01 mole), and sodium acetate (0·01 mole) in acetic anhydride (15 ml.) were refluxed for 10 min. The *dye* was filtered off from the chilled solution, washed with water, and recrystallized. (*b*) The 1-2′-carboxyphenyl-2-(3-ethylbenzothiazolin-2-ylidene)ethylidene dye (IX; R = H) (0·01 mole) was refluxed for 5 min. in acetic anhydride (15 ml.). The dye was filtered off from the chilled solution.

2-(3-*Ethylbenzothiazolin*-2-*ylidene*)-3-(3-*ethyl*-4-*oxo*-2-*thio*-*oxazolidin*-5-*ylidene*)*indan*-1-*one* (VII; ring A = 3-ethyl-2-thio-oxazolid-4-one) was obtained in 60% yield by method (*a*) as brick-red leaflets, m. p. 260°, from chloroform–light petroleum (Found: N, 6·3; S, 14·9. $C_{23}H_{18}N_2O_3S_2$ requires N, 6·4; S, 14·8%). It had $\lambda_{max.}$ 425 and 500 mμ, (log ε 4·30 and 4·23).

2-(3-*Ethylbenzothiazolin*-2-*ylidene*)-3-(3-*ethyl*-4-*oxo*-2-*thiothiazolidin*-5-*ylidene*)*indan*-1-*one* (VII; ring A = 3-ethyl-2-thiothiazolid-4-one) was obtained in 74% yield by method (*a*) as sepia rosettes, m. p. 219°, from chloroform–light petroleum (Found: N, 6·1; S, 21·3. $C_{23}H_{18}N_2O_2S_3$ requires N, 6·2; S, 21·3%), $\lambda_{max.}$ 540 and 425 mμ, (log ε 4·30 and 4·20). The same dye was obtained in 65% yield by method (*b*).

Merocyanines with an o-*Carboxyphenyl Substituent in the Chain* (X) (*Table* 5).—The 2-(β-acetoxy-2-carboxystyryl)-3-ethylthiazolium salt (IV; R = Me) (0·01 mole) or the related benzoyloxy- (IV; R = Ph) or methoxy-salt (V) (0·01 mole), a ketomethylene dye intermediate (0·01 mole), and triethylamine (0·02 mole) in ethanol (15 ml.) were refluxed for 10 min. The dye crystallized from the cooled, acidified solution.

TABLE 5.

Dimethinemerocyanines with an *o*-carboxyphenyl substituent in the chain (X; *n* = 0).

Ring B	Yield (%)	M. p.	$\lambda_{max.}$	log ε	Found (%) N	Found (%) S	Formula	Required (%) N	Required (%) S
(i) *Ring A = benzothiazoline*									
3-Phenyl-2-thio-oxazolid-4-one	24 *	121°	512	4·61	5·4	13·0	$C_{27}H_{20}N_2O_4S_2$	5·6	12·8
3-Ethyl-2-thiothiazolid-4-one	85 †	235	543 i518	4·96 4·69	6·1	21·4	$C_{23}H_{20}N_2O_3S_3$ §§	6·2	21·4
3-Ethoxycarbonylmethyl-2-thiothiazolid-4-one	75 ‡	179	543 i515	5·01	5·3	18·1	$C_{25}H_{22}N_2O_5S_3$	5·3	18·3
3-Methyl-1-phenylpyrazol-5-one	79 §	247 ‡‡	497	4·82	8·7	6·7	$C_{28}H_{23}N_3O_3S$	8·7	6·7
(ii) *Ring A = 5-chlorobenzothiazoline*									
3-Ethoxycarbonylmethyl-2-thiothiazolid-4-one	79 ¶	242	543 i514	4·99	4·9	17·2	$C_{25}H_{21}ClN_2O_5S_3$	5·0	17·1
(iii) *Ring A = naphtho*[1,2-d]*thiazoline*									
3-Ethyl-2-thio-oxazolid-4-one	32 **	206 ‡‡	523	4·68	5·6		$C_{27}H_{22}N_2O_4S_2$	5·6	
3-Ethoxycarbonylmethyl-2-thiothiazolid-4-one	83 ††	245	558 i530	5·12 4·78	4·8	16·6	$C_{29}H_{24}N_4O_5S_3$	4·9	16·7

* Brick powder from benzene–light petroleum. † Blue prisms from acidified ethanol. ‡ Maroon needles from benzene–ethanol–light petroleum. § Orange leaflets from ethanol. ¶ Sepia leaflets from ethanol. ** Green prisms from methanol–ethyl acetate–light petroleum. †† Green powder from acidified ethanol. ‡‡ Decomp. §§ Found: C, 61·6; H, 4·4. Reqd.: C, 61·5; H, 4·5%.

5-[3-o-*Carboxyphenyl*-4-(3-*ethylbenzothiazolin*-2-*ylidene*)*but*-2-*enylidene*]3-*ethoxycarbonylmethyl*-2-*thiothiazolid*-4-*one* (X; ring A = benzothiazoline; ring B = 3-ethoxycarbonylmethyl-2-thiothiazolid-4-one; *n* = 1) was obtained as a blue powder, m. p. 196°, from benzene–light petroleum in 50% yield (Found: N, 4·9. $C_{27}H_{24}N_2O_5S_3$ requires N, 5·1%). It had $\lambda_{max.}$ 637 mμ (log ε 4·93) with an inflection at 602 mμ.

Bis-(3-*ethyl*-2-*benzothiazole*)-β-o-*carboxyphenyltrimethinecyanine Iodide* (VI; X = I).—2-(β-Acetoxy-2-carboxystyryl)-3-ethylbenzothiazolium bromide (IV; R = Me, X = Br) (2·2 g., 0·005 mole), 3-ethyl-2-methylbenzothiazolium iodide (1·5 g., 0·005 mole), and triethylamine (1·4 ml., 0·01 mole) in ethanol (15 ml.) were refluxed for 15 min. The cooled solution was acidified with dilute hydrochloric acid. The *product* which separated was filtered off and recrystallized from ethanol as blue-green prisms, m. p. 220° (decomp.) (1·2 g., 39%) (Found: N, 4·6; S, 10·6. $C_{28}H_{25}IN_2O_2S_2$ requires N, 4·6; S, 10·5%). It was identical with the dye prepared by Brooker and Sprague.[1]

3-*Ethoxycarbonylmethyl*-5-[1-o-*ethoxycarbonylphenyl*-2-(3-*ethylbenzothiazolin*-2-*ylidene*)-*ethylidene*]-2-*thiothiazolid*-4-*one* (IX; ring A = 3-ethoxycarbonylmethyl-2-thiothiazolid-4-one R = Et).—The dimethinemerocyanine dye (IX; ring A = 3-ethoxycarbonylmethyl-2-thiothiazolid-4-one; R = H) (1·5 g.) was refluxed for 1 hr. in saturated ethanolic hydrochloric acid (80 ml.). The solution was concentrated and poured into water. The *product* was filtered off and recrystallized from benzene–light petroleum as maroon crystals, m. p. 195° (1·2 g., 76%) (Found: C, 58·6; H, 4·8; N, 5·1; S, 17·4. $C_{27}H_{26}N_2O_5S_3$ requires C, 58·5; H, 4·7; N, 5·1; S, 17·3%), $\lambda_{max.}$ 543 mμ (log ε 4·90).

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[*Received, May 20th,* 1963.]