941. *Oxazole Cyanine and* mero*Cyanine Dyes, and Intermediates.*

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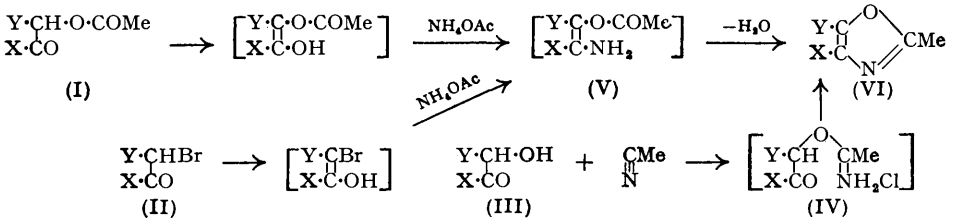
A direct synthesis of 2-methyl-4-(or 4 : 5-di-)substituted oxazoles from phenacyl bromides and ammonium acetate has been achieved. The syntheses due to Japp and Murray and to Davidson *et al.* have been extended to 4 : 5-dialkyl- and 4-aryl-oxazoles respectively. These oxazoles, together with 2-methyloxazole, have been quaternised and converted into cyanine and *mero*cyanine dyes. A comparison of the dye absorption maxima throws some light on to the spatial configuration of 4- and 5-aryl substituents in the oxazole nucleus. In the Davidson synthesis of diaryloxazoles, prolonging the reaction period slowly converts the oxazoles into the corresponding glyoxalines.

In parallel with an investigation into the chemical and photographic properties of substituted thiazole dyes (Knott, *J.*, 1952, 4099) it was considered of value to prepare and examine the 4 : 5-disubstituted oxazole analogues. The cyanines and *mero*cyanines, which were also useful as intermediates for more complex trinuclear dyes (cf. B.I.O.S. Final Report No. 1355, Item No. 22), proved to be strong sensitisers.

The preparation of 2-methyloxazole by Cornforth and Cornforth (*J.*, 1947, 96) enabled us to derive the simplest dyes of the series. A general oxazole synthesis by dehydrating

the related α-acylamino-carbonyl compounds (Zinsstag and Prijs, *Helv. Chim. Acta*, 1949, **32**, 147; Gabriel, *Ber.*, 1910, **43**, 1283) was used to synthesise 5-aryl-2-methyloxazoles. The 4- and 4 : 5-substituted analogues were obtained by modifications of a general reaction between α-acetoxy- (I), α-bromo- (II), and α-hydroxy-ketones (III) with ammonium acetate (Davidson, Weiss, and Jelling, *J. Org. Chem.*, 1937, **2**, 328), acetamide (Blümlein, *Ber.*, 1884, **17**, 2578; Lewy, *Ber.*, 1887, **20**, 2576; 1888, **21**, 924), or acetonitrile (Japp and Murray, *J.*, 1893, **63**, 469). The procedure of Davidson *et al.* and of Japp and Murray was extended to the synthesis of a 2 : 4-substituted and a 2 : 4 : 5-trialkyl-oxazole respectively. As an alternative to Davidson's method oxazoles were obtained from phenacyl bromides (II; X = aryl, Y = H or aryl) and ammonium acetate in acetic acid, the yields improving to 80—90% for (II; Y = aryl).



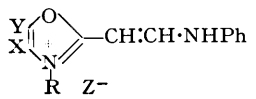
In attempts to prepare a possible intermediate acetiminodesyl ether hydrochloride (IV; X = Y = C_6H_5), hydrogen chloride was passed into a mixture of benzoin and acetonitrile according to Pinner's synthesis (*Ber.*, 1878, **11**, 6, 152) of simple imino-ethers. Various solvents were used, including benzene and acetic acid. However, even prolonged boiling of the reagents in acetic acid failed to produce the intermediate.

As the reaction of phenacyl bromide with amides has been shown by Robinson (*J.*, 1909, **95**, 2167) to give 2 : 4-substituted oxazoles, the similar reaction between phenacyl bromide and ammonium acetate might be expected to result in substitution in the same positions. This was confirmed in the cases of 4-*p*-methoxyphenyl-2-methyl- and 4-*p*-methoxyphenyl-2-methyl-5-phenyl-oxazole which were prepared by the latter method, and also by that of Davidson *et al.*, whose synthesis is unambiguous and allows ring closure resulting in 4-*p*-methoxyphenyl substitution. An intermediate amino-compound (V; X = Y = 2′-furyl) of the type suggested by Wiley (*Chem. Reviews*, 1945, **37**, 410) was isolated from the preparation of 4 : 5-di-2′-furyl-2-methyloxazole from 2 : 2′-furoin acetate and ammonium acetate after 1 hour's refluxing in acetic acid. This was the only case in which evidence of an intermediate amine was obtained. In an attempt to prepare 2-methyl-4 : 5-di-2′-thienyloxazole by an analogous reaction, the reaction time in acetic acid was increased to 2 hours, to reduce the amount of intermediate amine formed. The products, which were precipitated together as an oil when the acid reaction solution was poured into water, proved to be the required oxazole and 2-methyl-4 : 5-di-2′-thienylglyoxaline in 28 and 18% yield respectively. Davidson *et al.* have shown that glyoxalines can be obtained in low yields by making alkaline the aqueous solution into which the acetic acid reaction mixture has been poured. These authors have put forward a mechanism of formation *via* intermediates (V), (VII*a*) and (VII*b*), giving as evidence the formation of a glyoxaline

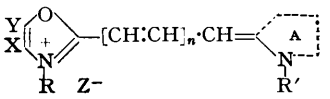
from (VII*b*; R = H) and ammonia. It has now been found that by prolonging the reaction period of benzoin acetate and ammonium acetate in acetic acid, the yields of oxazole and glyoxaline after 1 hour are 85% and 8%, and after 8 hours are 80 and 13·7%. Further, when 2-methyl-4 : 5-diphenyloxazole is heated under reflux in acetic acid with ammonium acetate for 4 days, a 37% yield of 2-methyl-4 : 5-diphenylglyoxaline is obtained. These facts indicate that, although there may be some initial formation from acyclic intermediates, longer reaction periods favour glyoxaline formation by fission of the oxazole ring, and further nitrogen substitution. Examples of glyoxalines produced from oxazoles and ammonia are known (Lewy, *Ber.*, 1888, **21**, 2192; Japp and Murray, *loc. cit.*; Minovici,

Ber., 1896, **29**, 2097), but the conditions of formation were far more vigorous, involving sealed tubes at high temperatures.

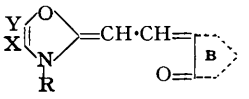
All the oxazole bases prepared above were quaternised with alkyl toluene-*p*-sulphonates and the mainly water-soluble products condensed with ethyl*iso*formanilide (cf. Knott, *J.*, 1946, 120) to give 2-2′-anilinovinyloxazole salts (VIII), or treated directly with dye intermediates. Although 2 : 2′-anilinovinyl-4-aryloxazole quaternary salts did not fluoresce, 5-aryl- and 4 : 5-di-aryl analogues glowed in daylight, and emitted an intense yellow-green fluorescence in ultra-violet light. Preparation of *mero*cyanines (X) and symmetrical carbocyanines were carried out by acetylation of the anilinovinyl intermediates, and condensation of the product with dye intermediates according to well-known methods.



(VIII)



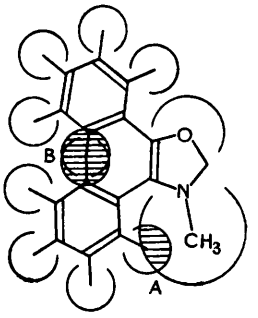
(IX)



(X)

Many of the 4 : 5-diaryl substituted dyes were more soluble in organic solvents than were corresponding dyes derived from benzoxazole, notwithstanding their increased molecular weight, and there was also a marked increase in the solubility of 4-aryl-substituted dyes compared with their 5-aryl isomers. The absorption maxima of isomeric dyes also varied with the position of substitution in the oxazole ring.

4-Aryl substitution of oxazole dyes increases the wave-lengths of the absorption maxima appreciably, and both 5-aryl and 4 : 5-diaryl substitution cause very marked increases, the effects in the last two cases being of the same order for corresponding dyes. Thus, for dyes of types (IX and X), the bathochromic shift on 4-phenyl substitution is 1—9 mμ, and for the 5-phenyl and 4 : 5-diphenyl analogues it is 22—29 and 20—30 mμ respectively. These results imply that the $-M$ effect of the 5-aryl group has a considerable contribution to make towards the resonance hybrid of the molecule, whereas the 4-aryl group has only a slight influence, which is almost entirely masked in the 4 : 5-substituted dyes. One may interpret the variations by supposing that the 5-aryl group is coplanar with the oxazole ring, and the 4-aryl group is crowded out by a twisting of the C–C bond between the aryl ring and the oxazole ring, as is demonstrable in models. The crowded areas *A* and *B* are shown in the Figure. Support for this reasoning is derived by observation that the values for the absorption maxima of dyes of type (IX; $n = 0$) and of symmetrical carbocyanines are the same for 4-methyl or 4-phenyl derivatives (Brooker, Keyes, and White, *J. Amer. Chem. Soc.*, 1935, **57**, 2492; Sachi Taki, *Rep. Sci. Res. Inst., Japan*, 1949, **25**, 224). Also the absorption maximum of the carbocyanine from planar benzoxazole is 485 mμ (Hamer, *J.*, 1934, 2796), which is closer to the value for the corresponding 5-phenyloxazole dye (500 mμ) than to that for its 4-phenyl isomer (460 mμ).



As would be expected if the molecule is non-planar, substituents such as 4-methoxy or 3 : 4-dimethoxy in the 4-aryl ring produce no marked difference in $\lambda_{max.}$, and even a 4-dimethylamino-group causes an average bathochromic shift of only 9 mμ.

Kiprianov and Ushenko (*J. Gen. Chem., U.S.S.R.*, 1950, **20**, 139) have pointed out that the solubility effect mentioned previously is associated with non-planarity of the dye molecule. They have also stated that other phenomena which may be observed include decreased stability towards acids and alkalis, ineffective photographic sensitivity, and reduced dye intensity. None of these properties is exhibited by the present dyes since the non-planarity is extra-nuclear and the main resonance system is undistorted.

Of the other oxazole dyes examined, the effect of 4 : 5-di-2′-furyl and 4 : 5-di-2′-thienyl groups was of the same order as that of 4 : 5-diphenyl, whereas 4 : 5-di-2′-naphthyl increased the wave-length of absorption maxima appreciably compared with that of its 4 : 5-diphenyl analogues.

Experimental

(Analyses were by Drs. Weiler and Strauss, Oxford. M. p.s are uncorrected.)

β-*Naphthoin Acetate.*—To a mixture of β-naphthoin (Fulton and Robinson, *J.*, 1939, 200) (12·6 g.), acetic acid (10 c.c.), and acetic anhydride (10 c.c.) was added sulphuric acid (1 c.c.), with cooling and shaking. The mixture was warmed for 10 minutes on the steam-bath, cooled, and poured into water (120 c.c.). An oil separated, which was extracted with ether. This solution was dried (Na_2SO_4) and used for preparation of 2-methyl-4 : 5-di-2′-naphthyloxazole.

2 : 2′-*Thienoin Acetate.*—2 : 2′-Thienoin (Cardon and Lankelma, *J. Amer. Chem. Soc.*, 1948, **70**, 4248) (8·6 g.) and acetic anhydride (35 c.c.) were refluxed for 1 hour. The solvent was distilled off under a vacuum, and the *product* crystallised on addition of a small amount of alcohol to the gum. It recrystallised as plates (9·5 g., 93%), m. p. 103°, from ethanol (Found: S, 23·9. $C_{12}H_{10}O_3S_2$ requires S, 24·0%).

Attempts to Prepare α-1-*Iminoethoxydeoxybenzoin Hydrochloride* (IV; X = Y = Ph).—Benzoin (10·6 g., 1 mol.) and acetonitrile (2·05 g., 1 mol.) in ether (100 c.c.) were saturated with hydrogen chloride and kept overnight. The solvent was removed, leaving benzoin (10·4 g.) which, recrystallised from ethanol, had m. p. 136°. Use of benzene and refluxing gave the same result.

Passing hydrogen chloride into the reagents in boiling acetic acid (100 c.c.) for 3 hours and removing the solvent produced a gum, which on extraction with ether gave benzoin acetate (7 g.) which, recrystallised from methanol and light petroleum, had m. p. 82°.

4 : 5-*Substituted 2-Methyloxazoles.*—*Method A* (cf. Davidson, Weiss, and Jelling, *J. Org. Chem.*, 1937, **2**, 328). An aryloin acetate (1 mol.), ammonium acetate (5 mols.), and acetic acid (1 l.) were refluxed for 1 hour, and the solution was cooled and poured into water (3·8 l.). The oil which separated was extracted with benzene, washed with aqueous sodium carbonate, and dried (Na_2SO_4). After removal of the benzene, the oxazole was distilled under a vacuum.

Method B. A substituted ω-bromoacetophenone (1 mol.), ammonium acetate (4 mols.), and acetic acid (1·5 l.) were refluxed for 1·5 hours, and the solution was cooled and poured into water (5 l.). The oxazole was worked up as in Method A.

Method C (cf. Japp and Murray, *J.*, 1893, **63**, 469). A mixture of an acyloin or aryloin (1 mol.) and acetonitrile (2·6 mols.) was added slowly to sulphuric acid (500 c.c.), at $<60°$ (cooling). The mixture was left overnight, then poured into water and crushed ice (3·5 l.), made alkaline with sodium carbonate, and extracted with chloroform. After drying (Na_2SO_4), the chloroform was distilled off, and the oxazole was distilled if an oil, or recrystallised if a solid.

2-*Amino*-1 : 2-*di*-2′-*furylvinyl Acetate.*—In the preparation of 4 : 5-di-2′-furyl-2-methyloxazole by Method A, after 2 : 2′-furoin acetate (Fisher, *Annalen*, 1882, **211**, 220) had been refluxed with ammonium acetate in acetic acid for 1 hour and the solution poured into water, a solid separated. This was dissolved in ether, and hydrogen chloride passed into the solution. An alcoholic solution of the hydrochloride thus formed was dropped into aqueous sodium carbonate. The *acetate* so formed was filtered off and crystallised from benzene as a buff powder (2 g.), m. p. 136° (Found: C, 62·0; H, 4·6; N, 6·1. $C_{12}H_{11}O_4N$ requires C, 62·0; H, 4·7; N, 6·0%).

Hydrogen chloride was passed into the benzene filtrate, precipitating a white hydrochloride. This was crystallised from ethanol–ether, dissolved in alcohol, and dropped into aqueous carbonate solution. 4 : 5-Di-2′-furyl-2-methyloxazole separated as a buff granular solid.

2-*Methyl*-4 : 5-*di*-2′-*thienylglyoxaline.*—Pouring the di-2′-thienyloxazole reaction solution (Method A, 2 hours' reflux) into water gave an oil, which was dissolved in ether, dried, and precipitated as hydrochloride. This solid was dissolved in alcohol, and poured into aqueous carbonate solution, liberating a mixture of glyoxaline and oxazole as an oil. On extraction with cold benzene, the oxazole dissolved, leaving as a solid the *glyoxaline*, which crystallised from benzene as pale grey-brown needles, m. p. 188° (18%) (Found: C, 58·5; H, 4·2; N, 11·4; S, 25·9. $C_{12}H_{10}N_2S_2$ requires C, 58·6; H, 4·1; N, 11·4; S, 26·0%).

Reactions of Benzoin Acetate and 2-*Methyl*-4 : 5-*diphenyloxazole with Ammonium Acetate.*—(*a*) Benzoin acetate (28·4 g., 1 mol.) and ammonium acetate (38·5 g., 5 mols.) in acetic acid (100 c.c.) were refluxed for 1 hour, and then poured into water (380 c.c.). The oil which separated was extracted with benzene, washed with aqueous sodium carbonate, and dried (Na_2SO_4). After removal of the benzene by distillation, 2-methyl-4 : 5-diphenyloxazole distilled (b. p. 227—228°/12 mm.) in 85% yield. Making the aqueous layer alkaline precipitated 2-methyl-4 : 5-diphenylglyoxaline (1·9 g., 8·1%), which formed needles, m. p. 239°, from ethyl acetate.

(*b*) When the reaction period was 8 hours, the yields of oxazole and glyoxaline were 18·8 g. (80%) and 3·2 g. (13·7%) respectively.

TABLE 1. 4 : 5-*Substituted* 2-*methyloxazoles* (VI).

X	Y	Method of prepn.*	Yield (%)	M. p. or b. p. (°/mm.)	Formula	Found: N, %	Reqd.: N, %
H	H	D	74	87—88	—	—	—
Ph	H	E	—	46	—	—	—
p-MeO·C_6H_4	H	A	49	100—101 [e]	$C_{11}H_{11}O_2N$	7·3	7·4
		B	42 [a]				
H	Ph	F	33	58	—	—	—
H	*p*-MeO·C_6H_4	F	16	94 [f]	$C_{11}H_{11}O_2N$	7·5	7·4
Pr^n	Pr^n	C	31 [b]	80/16 [g]	$C_{10}H_{17}ON$	8·5	8·4
2′-Furyl	2′-Furyl	A	29	56—58 [h]	$C_{12}H_9O_3N$	·6·2	6·5
2′-Thienyl	2′-Thienyl	A	28	oil	—	—	—
Ph	Ph	A	85	28	—	—	—
		C	85				
β-$C_{10}H_7$	β-$C_{10}H_7$	A	49	69—72 [i]	—	—	—
p-MeO·C_6H_4	Ph	A	77	227—228/12	$C_{17}H_{15}O_2N$	5·2	5·3
		B	87 [c]				
p-NMe_2·C_6H_4	Ph	C	60	108 [j]	$C_{18}H_{18}ON_2$	9·9	10·1
3 : 4 : 1-$(MeO)_2C_6H_3$	Ph	B	85 [d]	16 [k]	—	—	—

* A, B, C, see text; D, Cornforth and Cornforth; E, Blümlein; F, Zinsstag and Prijs, *locc. cit.* [a] From ω-bromo-*p*-methoxyacetophenone (Cowper and Davidson, *Org. Synth.*, **19**, 24). [b] From *n*-butyroin (Snell and McElvain, *Org. Synth.*, **13**, 24). [c] From α-bromo-4-methoxydeoxybenzoin (Meisenheimer and Jochelson, *Annalen*, 1907, **355**, 292). [d] From α-bromo-3 : 4-dimethoxydeoxybenzoin (Kaufmann and Muller, *Ber.*, 1918, **51**, 129). [e] Needles, from ligroin. [f] Prisms, from light petroleum. [g] Pyridine-like odour. [h] Buff granular solid, from light petroleum. [i] Amorphous, from ligroin. The *hydrochloride* forms prisms (from methanol–ether), m. p. 220° (Found: Cl, 9·4. $C_{21}H_{17}ON$,HCl requires Cl, 9·6%). [j] Needles, from ethanol. [k] The *hydrochloride* forms needles (from ethanol–ether), m. p. 179° (decomp.) (Found: N, 4·2. $C_{18}H_{17}O_3N$,HCl requires N, 4·2%).

(*c*) 2-Methyl-4 : 5-diphenyloxazole (23·5 g., 1 mol.) and ammonium acetate (38·5 g., 5 mols.) in acetic acid (100 c.c.) were refluxed for 4 days, giving 12·3 g. (52·5%) of oxazole and 8·7 g. (37·2%) of glyoxaline.

2-*Methyl*-4 : 5-*diphenyloxazole Ethotoluene*-p-*sulphonate*.—2-Methyl-4 : 5-diphenyloxazole (4·7 g., 1 mol.) and ethyl toluene-*p*-sulphonate (4·4 g., 1·1 mols.) were heated (oil-bath) at 140° for 2 hours. When the resultant thick oil was heated with ether, it crystallised; it recrystallised from ethanol–ether as colourless deliquescent prisms. Other quaternary salts listed in Table 2 were prepared by the same method, the time of heating and the temperature being varied.

4-p-*Dimethylaminophenyl*-2-*methyl*-5-*phenyloxazole Ethoperchlorate*.—4-*p*-Dimethylaminophenyl-2-methyl-5-phenyloxazole (27·8 g.) and ethyl toluene-*p*-sulphonate (20·0 g.) were heated together at 100° for 2 hours. On cooling the mixture solidified. It was dissolved in a little ethanol and poured into aqueous potassium perchlorate solution. The quaternary *salt* separated and was recrystallised several times from ethanol–ether, being obtained as pale buff needles, m. p. 162° (Found: N, 6·9; Cl, 8·5. $C_{20}H_{23}O_5N_2Cl$ requires N, 6·9; Cl, 8·7%). The same oxazole (2·78 g., 1 mol.) and ethyl toluene-*p*-sulphonate (4·0 g., 2 mols.) were heated at 140° for 1 hour. The residual diquaternary salt was ground with ether to give a white deliquescent powder which was not further purified. Methyl toluene-*p*-sulphonate gave a similar product.

2-2′-*Anilinovinyl*-4 : 5-*diphenyloxazole Ethotoluene*-p-*sulphonate*.—2-Methyl-4 : 5-diphenyloxazole ethotoluene-*p*-sulphonate (8·7 g., 1 mol.) and ethyl*iso*formanilide (3·3 g., 1·1 mols.) were heated at 140° for 1 hour (cf. Knott, *loc. cit.*). Ethanol was evolved, and on cooling, the thick oily *product* solidified. It recrystallised from ethanol–ether as fluorescent lemon-yellow needles, m. p. 209° (10 g.) (Found: N, 5·2. $C_{32}H_{30}O_4N_2S$ requires N, 5·2%). The other 2-2′-anilinovinyl quaternary *salts* listed in Table 2 were prepared by the same procedure.

4 : 5-*Substituted* 2-2′-*Acetanilidovinyloxazole Ethotoluene*-p-*sulphonates*.—The anilinovinyl quaternary salts were acetylated by an excess of boiling acetic anhydride for 0·25—4 hours. The solvent was then distilled off at the pump, and the gummy products were used to prepare dyes.

2-p-*Dimethylaminostyryl*-4 : 5-*diphenyloxazole Ethoperchlorate*.—2-Methyl-4 : 5-diphenyloxazole ethotoluene-*p*-sulphonate (2·2 g.) and *p*-dimethylaminobenzaldehyde (0·8 g.) were dissolved in ethanol (12 c.c.), and a drop of piperidine was added. After 1 hour's heating on the steam-bath the solution was poured into aqueous potassium perchlorate. An oily *salt* separated, and the aqueous layer was decanted. On addition of a little methanol, the oil solidified; it

TABLE 2. 2-2′-*Anilinovinyloxazolium salts* (VIII; R = Et, Z = p-$C_6H_4Me{\cdot}SO_3^-$).

		Prepn. of 2-methyl-oxazolium salts			Anilinovinyl salts						Found:	Reqd.:
X	Y	Reaction time (hr.)	Bath-temp.	Appear-ance	Reaction time (hr.)	Bath-temp.	Yield (%)	M. p.	Appearance	Formula	N, %	N, %
H	H	1	140	Prisms	0·5	140	94	147°	Bright straw plates	$C_{20}H_{22}O_4N_2S$	7·3	7·3
Ph	H	6	150	Solid	1	140	71	176	Orange prisms	$C_{26}H_{26}O_4N_2S$	6·1	6·1
p-MeO·C_6H_4	H	2	140	Glass	2	150	60	185	Bright amber plates	$C_{27}H_{28}O_5N_2S$	5·6	5·7
H	Ph	1	140	Needles	0·5	130	96	177	Yellow needles [2]	$C_{26}H_{26}O_4N_2S$	6·1	6·1
H	p-MeO·C_6H_4	1·5	130	Glass	1	130	88	201	Yellow leaflets [2]	$C_{27}H_{28}O_5N_2S$	5·5	5·7
Pr^n	Pr^n	2	120	Solid *	—	—	—	—	—	—	—	—
2′-Furyl	2′-Furyl	1	150	Gum	1	140	51	227	Orange needles [2]	$C_{28}H_{26}O_6N_2S$	5·2	5·4
2′-Thienyl	2′-Thienyl	1	140	Gum	0·2	140	98	196	Olive-green needles [3]	$C_{28}H_{26}O_4N_2S_3$	5·0	5·1
Ph	Ph	2	140	Needles	1	140	94	209	Lemon-yellow needles [2]	$C_{32}H_{30}O_4N_2S$	5·2	5·2
β-$C_{10}H_7$	β-$C_{10}H_7$	1	170	Solid	1	150	96	226	Yellow prisms [2]	$C_{40}H_{34}O_4N_2S$	4·5	4·4
p-MeO·C_6H_4	Ph	1·5	170	Glass	0·3	140	97	230	Lemon-yellow needles [2]	$C_{33}H_{32}O_5N_2S$	5·0	4·9
p-NMe_2·C_6H_4	Ph	2	100	Prisms [1]	2	150	72	—	Deliquescent yellow	—	—	—
p-C_6H_4·NMe_3Z	Ph	1	140	Solid	1	140	—	—	Deliquescent yellow	—	—	—
3 : 4 : 1-$(MeO)_2C_6H_3$	Ph	3	130	Prisms	1	140	92	228	Yellow needles [2]	$C_{34}H_{34}O_6N_2S$	4·7	4·7

* 2-Methyl-4 : 5-di-*n*-propyloxazole was quaternised with methyl toluene-p-sulphonate. This quaternary salt did not react with ethyl*iso*formanilide under the conditions used. [1] Perchlorate. [2] Fluoresced moderately in sunlight, intensely in ultra-violet light. [3] Found: S, 17·4. Reqd.: S, 17·5%.

TABLE 3. [1-R′-2-*Quinoline*][3-R-4-X-5-Y-2-*oxazole*]*methincyanine dyes* (IX; n = 0, A = 2-*quinoline*).

X	Y	R	R′	Z^-	Cryst. from	Yield (%)	M. p.	Appearance	$\lambda_{max.}$ (MeOH, mμ)	$10^{-4}\epsilon_{max.}$	Formula	Found, %	Reqd., %
H	H	Et	Me	ClO_4	MeOH	40	235° [a]	Mustard prisms	430(415i)	3·49	$C_{16}H_{17}O_5N_2Cl$	N, 7·9	7·95
Pr^n	Pr^n	Me	Me	ClO_4	EtOH	—	200	Orange needles	435	3·2	$C_{21}H_{27}O_5N_2Cl$	Cl, 8·5	8·4
Ph	Ph	Et	Me	I	MeOH	76	286 [b]	,,	452	4·1	$C_{28}H_{25}ON_2I$	I, 23·6	23·9
p-MeO·C_6H_4	Ph	Et	Et	ClO_4	EtOH	27	227	,,	451	3·5	$C_{30}H_{29}O_6N_2Cl$	N, 5·0	5·1
,,	,,	,,	Me	ClO_4	C_5H_5N–MeOH	45	270	Orange prisms	458	2·1	$C_{29}H_{27}O_6N_2Cl$	N, 5·1	5·2
p-NMe_2·C_6H_4	Ph	Et	Me	I	EtOH	—	290	Red needles	470	3·4	$C_{30}H_{30}ON_3I$ [c]	N, 7·1	7·3
p-C_6H_4·NMe_3Z	Ph	Et	Me	I	Aq. EtOH	—	271	Orange needles	450	7·0	$C_{31}H_{33}ON_3I_2$	I, 35·2	35·4

[a] Darkens. [b] Decomp. [c] Found: I, 21·9. Reqd.: I, 22·1%.

TABLE 4. *Symmetrical trimethincyanine dyes: bis-*[3-R-4-X-5-Y-2-*oxazole*]*trimethincyanine perchlorates.*

R	X	Y	Cryst. from	Yield (%)	M. p. (decomp.)	Appearance (reflex)	$\lambda_{max.}$ (MeOH, mμ)	$10^{-4}\epsilon_{max.}$	Formula	Found, %	Reqd., %
Et	Ph	H	EtOH	—	226°	Orange needles (purple)	460	10·1	$C_{25}H_{25}O_6N_2Cl$	Cl, 7·3	7·3
Et	H	Ph	MeOH	—	221	Crimson leaflets	500	8·1	$C_{25}H_{25}O_6N_2Cl$	Cl, 7·2	,,
Et	H	p-MeO·C_6H_4	C_5H_5N–Et_2O	—	260	Orange	510(490i)	7·4	$C_{27}H_{29}O_8N_2Cl$	N, 5·0	5·1
										Cl, 6·5	6·5
Et	Ph	Ph	C_5H_5N–EtOH–Et_2O	49	242	Brown prisms (green)	504(486i)	4·3	$C_{37}H_{33}O_6N_2Cl$	N, 4·4	4·4
Et	p-MeO·C_6H_4	Ph	EtOH	10	220 [a]	Orange-brown	507(486i)	8·2	$C_{39}H_{37}O_8N_2Cl$	N, 4·0	4·0
Et	3 : 4 : 1-$(MeO)_2C_6H_3$	Ph	C_5H_5N–Et_2O	30	237	Orange leaflets (gold)	510(486i)	12·8	$C_{41}H_{41}O_{10}N_2Cl$	N, 3·7	3·7
										Cl, 4·8	4·7

[a] No decomp.

TABLE 5. [3-R-4-X-5-Y-2-*Oxazole*][3-*ethyl*-2-*benzoxazole*]*trimethincyanine dyes* (IX; $n = 1$, A = 2-*benzoxazole*).

R	X	Y	Z^-	Cryst. from	Yield (%)	M. p.	Appearance	$\lambda_{max.}$ (MeOH, mμ)	$10^{-4}\epsilon_{max.}$	Formula	Found, %	Reqd., %
Et	H	H	ClO_4	MeOH	33	236° [a]	Orange-brown leaflets	460(444i)	9·1	$C_{17}H_{19}O_6N_2Cl$	N, 7·3	7·3
Et	Ph	H	ClO_4	EtOH	71	192	Bright-maroon plates	469(457i)	6·9	$C_{23}H_{23}O_6N_2Cl$	Cl, 7·5	7·7
Et	*p*-MeO·C_6H_4	H	ClO_4	,,	—	259 [b]	Orange-red	482(468i)	12·5	$C_{24}H_{25}O_7N_2Cl$	Cl, 7·2	7·3
Et	H	Ph	ClO_4	,,	—	159	Orange leaflets	489	5·7	$C_{23}H_{23}O_6N_2Cl$	Cl, 7·9	7·7
Et	H	*p*-MeO·C_6H_4	I	,,	—	218	Orange	490(475i)	7·8	$C_{24}H_{25}O_3N_2I$	I, 24·5	24·7
Et	2-Furyl	2-Furyl	I	,,	56	209	Orange-brown	491	7·9	$C_{25}H_{23}O_4N_2I$	N, 5·0	5·2
Et	Ph	Ph	I	EtOH–Et_2O	—	145 [c]	Red prisms	490(474i)	8·3	$C_{29}H_{27}O_2N_2I$	I, 22·4	22·6
Et	*p*-MeO·C_6H_4	Ph	ClO_4	EtOH	44	168 [d]	Carmine-red prisms	491(474i)	7·9	$C_{30}H_{29}O_7N_2Cl$	N, 5·1	5·0
Et	*p*-NMe_2·C_6H_4	Ph	ClO_4	,,	16	252	Red prisms	488	—	$C_{31}H_{32}O_6N_3Cl$ [e]	N, 7·2	7·3
Et	*p*-C_6H_4·NMe_3Z	Ph	ClO_4	,,	—	276	Orange-red	497(478i)	9·6	$C_{33}H_{37}O_{10}N_3Cl_2$ [f]	N, 5·8	6·0
Et	3 : 4 : 1-$(MeO)_2C_6H_3$	Ph	ClO_4	,,	40	230	Orange-red needles	490(475i)	7·3	$C_{31}H_{31}O_8N_2Cl$	Cl, 6·0	6·0

[a] Darkens. [b] Decomp. [c] Softens at 140°. [d] Softens at 163°. [e] Found: Cl, 6·1. Reqd.: Cl, 6·1%. [f] Found: Cl, 10·1. Reqd.: Cl, 10·1%.

TABLE 6. *Miscellaneous unsymmetrical carbocyanine dyes* (IX; $n = 1$).

Dye [3-R-4-X-5-Y-*Oxazole*][3-*methyl*-2-*thiazoline*]*trimethincyanine salts.* R	X	Y	Z	Cryst. from	Yield (%)	M. p.	Appearance	$\lambda_{max.}$ (MeOH, mμ)	$10^{-4}\epsilon_{max.}$	Formula	Found, %	Reqd., %
Et	2-Furyl	2-Furyl	I	EtOH–Et_2O	20	205°	Sepia needles	469	5·5	$C_{20}H_{21}O_3N_2SI$	S, 6·4	6·4
Et	Ph	Ph	I	EtOH	—	241 (decomp.)	Orange-red needles	461(479i)	6·3	$C_{24}H_{25}ON_2SI$	I, 24·3	24·6
Et	*p*-MeO·C_6H_4	Ph	ClO_4	MeOH	58	203	Orange-brown leaflets	463	6·0	$C_{25}H_{27}O_6N_2SCl$	S, 5·9	6·2
Et	*p*-NMe_2·C_6H_4	Ph	ClO_4	EtOH	26	240	Orange prisms	476	4·8	$C_{26}H_{30}O_5N_3SCl$	N, 8·0	7·9
											Cl, 6·8	6·7
[3-*Ethyl*-4-p-*methoxyphenyl*-5-*phenyl*-2-*oxazole*][3-*ethyl*-4 : 5-*diphenyl*-2-*oxazole*]*trimethincyanine perchlorate*				MeOH	18	210	Dark orange	504(482i)	8·1	$C_{38}H_{35}O_7N_2Cl$	N, 4·2	4·2

TABLE 7. 3-*Ethyl*-5-(3-*ethyloxazolin*-2-*ylidene-ethylidene*)-2-*thio-oxazolid*-4-*ones* (X; B = 3-*ethyl*-2-*thio-oxazolid*-4-*one*).

X	Y	Cryst. from	Yield (%)	M. p.	Appearance	$\lambda_{max.}$ (MeOH, mμ)	$10^{-4}\epsilon_{max.}$	Formula	Found, %	Reqd., %
H	H	C_6H_6	—	149°	Orange needles	470	3·0	$C_{12}H_{14}O_3N_2S$	N, 10·4	10·5
Ph	H	EtOH	68	219	,,	471(458i)	5·4	$C_{18}H_{18}O_3N_2S$	S, 9·4	9·4
p-MeO·C_6H_4	H	,,	72	187	,,	472	6·9	$C_{19}H_{20}O_4N_2S$	N, 7·4	7·5
H	Ph	,,	34	200	,,	493(476i)	5·8	$C_{18}H_{18}O_3N_2S$	N, 8·4	8·2
H	*p*-MeO·C_6H_4	C_6H_6–pet [a]	41	219	Brick-red	490	6·4	$C_{19}H_{20}O_4N_2S$	N, 7·3	7·5
2′-Furyl	2′-Furyl	EtOH	—	213	Red-brown needles	487	5·4	$C_{20}H_{18}O_5N_2S$	N, 6·9	7·0
2′-Thienyl	2′-Thienyl	C_6H_6–pet [a]	—	248	Emerald-green prisms	490	6·8	$C_{20}H_{18}O_3N_2S_3$	N, 6·4	6·5
									S, 22·1	22·3
Ph	Ph	EtOH	58	232	Orange-red needles	490	8·9	$C_{24}H_{22}O_3N_2S$	S, 7·8	7·7
β-$C_{10}H_7$	β-$C_{10}H_7$	C_6H_6–pet [a]	—	136	Brick-red	500	7·0	$C_{32}H_{26}O_3N_2S$	N, 5·3	5·4
p-MeO·C_6H_6	Ph	,,	52	229	Maroon prisms	491	—	$C_{25}H_{24}O_4N_2S$	S, 6·7	6·9
3 : 4 : 1-$(MeO)_2C_6H_3$	Ph	,,	60	238	Orange prisms	490(478i)	6·2	$C_{26}H_{26}O_5N_2S$	N, 5·9	5·9

[a] Light petroleum (b. p. 60—80°).

TABLE 8. 3-n-*Alkyl*-5-(3-*ethyloxazolin*-2-*ylidene-ethylidene*)-1-*phenyl*-2-*thiohydantoins* * (X; B = 3-*alkyl*-1-*phenyl*-2-*thiohydantoin*).

X	Y	3-*n*-Alkyl group	Cryst. from [a]	Yield (%)	M. p.	Appearance	$\lambda_{max.}$ (mμ, MeOH)	$10^{-4}\epsilon_{max.}$	Formula	Found, %	Reqd., %
Ph	H	n-C_7H_{15}	Ligroin	—	135°	Orange needles	486	6·9	$C_{29}H_{33}O_2N_3S$	N, 8·6	8·6
p-MeO·C_6H_4	H	n-C_7H_{15}	EtOAc–pet	35	136	Orange	489	7·5	$C_{30}H_{35}O_3N_3S$	N, 8·3	8·1
H	Ph	n-C_7H_{15}	C_6H_6–pet	67	210	Brick-red	505	7·4	$C_{29}H_{33}O_2N_3S$	N, 8·8	8·6
H	p-MeO·C_6H_4	n-C_7H_{15}	,,	29	206	Brick-red	510(i)	6·8	$C_{30}H_{35}O_3N_3S$	N, 7·9	8·1
2′-Furyl	2′-Furyl	Et	MeOH	—	210	Purple prisms	501	6·4	$C_{26}H_{23}O_4N_3S$	N, 8·8	8·9
Ph	Ph	Et	C_6H_6–pet	—	237	Orange prisms	503(i)	7·9	$C_{30}H_{27}O_2N_3S$	N, 8·3	8·5
β-$C_{10}H_7$	β-$C_{10}H_7$	n-C_7H_{15}	,,	54	213	Red	510(i)	9·0	$C_{43}H_{41}O_2N_3S$	N, 6·3	6·3
p-MeO·C_6H_4	Ph	Et	,,	—	231	Maroon prisms	505(i)	7·1	$C_{31}H_{29}O_3N_3S$	N, 7·9	8·0
p-MeO·C_6H_4	Ph	n-C_7H_{15}	,,	—	265	Orange needles	508(i)	9·2	$C_{36}H_{39}O_3N_3S$	N, 7·2	7·1
										S, 5·2	5·3
3 : 4 : 1-$(MeO)_2C_6H_3$	Ph	n-C_7H_{15}	EtOH	—	183	Orange-red	504(483i)	7·5	$C_{37}H_{41}O_4N_3S$	N, 6·7	6·7

* Prepared according to Brooker's method, U.S.P. 2,177,403. [a] Pet = light petroleum (b. p. 60—80°). Ligroin had b. p. 70—90°.

TABLE 9. 3-*Alkyl*-5(*and* 4)-(3-*ethyloxazolin*-2-*ylidene-ethylidene*)-2-*thiothiazolid*-4(*and* 5)-*ones* (X).

X	Y	Cryst. from [a]	Yield (%)	M. p.	Appearance	$\lambda_{max.}$ (mμ, MeOH)	$10^{-4}\epsilon_{max.}$	Formula	Found, %	Reqd., %
					From 3-*carboxymethyl*-2-*thiothiazolid*-4-*one*.					
Ph	Ph	EtOH	—	258°	Maroon leaflets	512(i)	8·0	$C_{24}H_{20}O_4N_2S_2$	S, 13·6	13·8
p-MeO·C_6H_4	Ph	MeOH	40	238	,,	513(i)	8·0	$C_{25}H_{22}O_5N_2S_2$	S, 13·0	12·9
					From 3-*ethyl*-2-*thiothiazolid*-4-*one*.					
2′-Furyl	2′-Furyl	C_6H_6–pet	70	211	Maroon needles	—	—	$C_{20}H_{18}O_4N_2S_2$	S, 15·3	15·4
Ph	Ph	,,	51	231	Red needles, blue reflex	514(i)	4·7	$C_{24}H_{22}O_2N_2S_2$	S, 14·6	14·7
β-$C_{10}H_7$	β-$C_{10}H_7$	,,	62	225	Green leaflets	521(i)	—	$C_{32}H_{26}O_2N_2S_2$	N, 5·2	5·2
p-MeO·C_6H_4	Ph	,,	82	205	Maroon needles	514(i)	8·0	$C_{25}H_{24}O_3N_2S_2$	S, 13·9	13·8
					From 3-*ethyl*-2-*thiothiazolid*-5-*one* (Jeffreys and Knott, *J.*, 1952, 4632).					
p-C_6H_4·NMe_2EtI	Ph	EtOH	—	233	Brown needles, green reflex	513(i)	9·1	$C_{28}H_{32}O_2N_3S_2I$	I, 20·0	20·1
β-$C_{10}H_7$	β-$C_{10}H_7$	C_6H_6–pet	10	247	Chocolate-brown	530(i)	—	$C_{32}H_{26}O_2N_2S_2$	N, 5·3	5·2
					From 3-cyclo*hexyl*-2-*thiothiazolid*-5-*one* (Jeffreys and Knott, *J.*, 1952, 4632).					
Ph	Ph	C_6H_6–pet	—	286	Red-bronze leaflets	522(i)	6·7	$C_{28}H_{28}O_2N_2S_2$	S, 12·9	13·1
p-NMe_2·C_6H_4	Ph	,,	—	286	Maroon needles, gold reflex	525	—	$C_{30}H_{33}O_2N_3S_2$	S, 11·9	12·0

[a] Pet = light petroleum (b. p. 60—80°).

TABLE 10. *Miscellaneous* mero*cyanine dyes* (X).

Dye	Cryst. from [a]	Yield (%)	M. p.	Appearance	$\lambda_{max.}$ (mμ, MeOH)	$10^{-4}\varepsilon_{max.}$	Formula	Found, %	Reqd., %
4-(3-Ethyl-4 : 5-di-2′-furyloxazolin-2-ylidene-ethylidene)-2-phenyl-oxazol-5-one	EtOH	20	205°	Maroon leaflets	499(476p)	7·5	$C_{24}H_{18}O_5N_2$	N, 6·9	6·8
4-(3-Ethyl-4 : 5-di-2′-furyloxazolin-2-ylidene-ethylidene)-2-ethyl-thiothiazol-5-one	MeOH	—	166	Green needles	504(478i)	5·7	$C_{20}H_{18}O_4N_2S_2$	S, 15·2	15·4
4-(3-Ethyl-4 : 5-diphenyloxazolin-2-ylidene-ethylidene)-2-ethyl-thiothiazol-5-one	EtOH	58	230	Red needles	502(481i)	7·7	$C_{24}H_{22}O_2N_2S_2$	S, 14·5	14·7
5-(3-Ethyl-4 : 5-diphenyloxazolin-2-ylidene-ethylidene)-2-diphenyl-aminothiazol-4-one	C_6H_6	—	203	Orange	493	2·8	$C_{34}H_{27}O_2N_3S$	S, 5·8	5·9
4-(3-Ethyl-4 : 5-diphenyloxazolin-2-ylidene-ethylidene)-3-methyl-1-phenylpyrazol-5-one	EtOH	36	246	Salmon-pink plates	449	5·0	$C_{29}H_{25}O_2N_3$	N, 9·3	9·4
1 : 3-Diethylhexahydro-4 : 6-diketo-5-(3-ethyl-4 : 5-diphenyloxazolin-2-ylidene-ethylidene)-2-thio-pyrimidine	EtOH–Et_2O	53	163	Orange-yellow needles	388(444i)	6·0	$C_{27}H_{27}O_3N_3S$,5EtOH	N, 5·9	6·0
4-(3-Ethyl-4-*p*-methoxyphenyl-5-phenyloxazolin-2-ylidene-ethylidene)-2-phenyloxazol-5-one	EtOH	78	218 (softens 210)	Red needles	501(474p)	8·2	$C_{29}H_{24}O_4N_2$	N, 5·9	6·0
4-(3-Ethyl-4-*p*-methoxyphenyl-5-phenyloxazolin-2-ylidene-ethylidene)-2-ethylthiothiazol-5-one	C_6H_6–pet	39	194	Maroon needles	500(482i)	6·2	$C_{25}H_{24}O_3N_2S_2$	S, 13·6	13·8
4-(3-Ethyl-4-*p*-methoxyphenyl-5-phenyloxazolin-2-ylidene-ethylidene)-3-methyl-1-phenylpyrazol-5-one	EtOH	34	191 (softens 132)	Orange-red needles	452	5·0	$C_{30}H_{27}O_3N_3$	N, 8·8	8·8
4-(3-Ethyl-4-*p*-methoxyphenyl-5-phenyloxazolin-2-ylidene-ethylidene)-3-methyl-1-*p*-sulphophenylpyrazol-5-one	$PhNO_2$	63	298	Mustard prisms	450	4·6	$C_{30}H_{27}O_6N_3S$	N, 7·3	7·3
5-(3-Ethyl-4-*p*-methoxyphenyl-5-phenyloxazolin-2-ylidene-ethylidene)-1: 3-diethylhexahydro-4 : 6-diketo-2-thiopyrimidine	EtOH	84	275	Yellow needles	442	3·6	$C_{28}H_{29}O_4N_3S$	N, 8·2	8·3

[a] Pet = Light petroleum (b. p. 60—80°).

crystallised from ethanol–ether as small orange prisms, m. p. 152° (Found: Cl, 7·1. $C_{27}H_{27}O_5N_2Cl$ requires Cl, 7·2%). It had $\lambda_{max.}$ 470 mμ in methanol.

4-p-*Dimethylaminophenyl*-2-p-*dimethylaminostyryl*-5-*phenyloxazole Ethoperchlorate*.—4-*p*-Dimethylaminophenyl-2-methyl-5-phenyloxazole ethoperchlorate (2·0 g.) and *p*-dimethylaminobenzaldehyde (0·8 g.) were dissolved in ethanol (10 c.c.) with a drop of piperidine. After 1 hour's heating on a steam-bath the solution was chilled, and the *dye* crystallised. It recrystallised from ethanol as red needles (orange reflex) (0·2 g.), m. p. 286° (Found: N, 7·7; Cl, 6·6. $C_{29}H_{32}O_5N_3Cl$ requires N, 7·8; Cl, 6·6%). It had $\lambda_{max.}$ 481 mμ in methanol.

[3-*Ethyl*-4 : 5-*diphenyl*-2-*oxazole*][1-*methyl*-2-*quinoline*]*methincyanine Iodide* (Table 3).—2-Methyl-4 : 5-diphenyloxazole ethotoluene-*p*-sulphonate (2·2 g., 1 mol.) and 2-methylthioquinoline methiodide (1·6 g., 1 mol.) with triethylamine (0·7 c.c., 1 mol.) in ethanol (15 c.c.) were heated for 15 minutes on the steam-bath. After chilling and filtration, the *dye* recrystallised from methanol as orange needles (2 g.), m. p. 286° (decomp.) (Found: I, 23·6. $C_{28}H_{25}ON_2I$ requires I, 23·9%). The *dyes* in Table 3 were prepared similarly.

Bis-[3-*ethyl*-4 : 5-*diphenyl*-2-*oxazole*]*trimethincyanine Perchlorate* (Table 4).—2-Methyl-4 : 5-diphenyloxazole ethotoluene-*p*-sulphonate (1·45 g., 1 mol.) and 2-2′-acetanilidovinyl-4 : 5-diphenyloxazole ethotoluene-*p*-sulphonate [prepared from the 2-2′-anilinovinyl compound (1·79 g., 1 mol.) and acetic anhydride] with triethylamine (0·5 c.c.) in ethanol (12 c.c.) were heated for 1 hour on the steam-bath. The solution was poured into aqueous potassium perchlorate. The *dye* was filtered off, washed with a little ethanol, and recrystallised from pyridine–ethanol–ether as brown prisms (green reflex) (0·7 g.), m. p. 242° (decomp.) (Found: N, 4·4. $C_{37}H_{33}O_6N_2Cl$ requires N, 4·4%). It had $\lambda_{max.}$ 507 mμ in methanol, with an inflection at 486 mμ. The *dyes* in Tables 4, 5, and 6 were prepared by the same method.

3-*Ethyl*-5-(3-*ethyl*-4 : 5-*diphenyloxazolin*-2-*ylidene*-*ethylidene*)-2-*thio*-*oxazolid*-4-*one* (Table 7).—2-2′-Acetanilidovinyl-4 : 5-diphenyloxazole ethotoluene-*p*-sulphonate [prepared from the 2-2′-anilinovinyl intermediate (2·68 g., 1 mol.) and excess of acetic anhydride] and 3-ethyl-2-thio-oxazolid-4-one (Ahlqvist, *J. pr. Chem.*, 1919, **99**, 60) (0·73 g., 1 mol.) with triethylamine (0·7 c.c.) in ethanol (15 c.c.) were refluxed for 15 minutes (cf. Brooker, U.S.P. 2,177,401). The solution was then chilled and filtered, and the *dye* washed with a little ethanol and crystallised from ethanol as long orange-red needles, m. p. 232° (Found: S, 7·8. $C_{24}H_{22}O_3N_2S$ requires S, 7·7%).

The *dyes* in Tables, 7, 8, 9, and 10 were prepared similarly. The *dyes* in Table 10 possessing a 2-ethylthiothiazol-5-one nucleus were prepared either by the above method or from the 4 : 5-substituted 2-methyloxazole quaternary salt and 4-ethoxymethylene-2-ethylthiothiazol-5-one (cf. Cook, Harris, and Shaw, *J.*, 1949, 1435; Aubert, Knott, and Williams, *J.*, 1951, 2185).

In Tables 3—10, " i " after the absorption maximum indicates an inflection, and in Table 10 " p " indicates a minor peak.

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