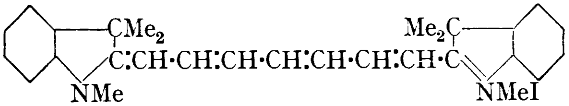
55. *Tricarbocyanines.*

By (Miss) Nellie I. Fisher and (Miss) Frances M. Hamer.

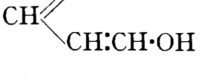
A recent advance in the chemistry of the cyanines is the preparation of various dicarbocyanines by Beattie, Heilbron, and Irving (J., 1932, 260). The present paper deals with the tricarbocyanines, in which the two heterocyclic nuclei are linked by the seven-carbon chain :CH·CH:CH·CH:CH·CH:CH. These substances were discovered independently by three sets of workers, of whom Wahl was the first in the field (G.P. 499,967/1928). Although his methods and ours are identical in theory, they differ considerably in practice, and he applied them only to tricarbocyanines of type (I), for which we propose the name *indotricarbocyanine*. This dye was also prepared by Imperial Chemical Industries Ltd., Piggott, and Rodd (B.P. 355,693/1930). Neither set of observers touched upon tricarbocyanines of any other type and we were unaware of their work until ours was well advanced and patents had been filed (Hamer and Ilford Ltd., B.P. 351,555/1930; 354,826/1930).

(I.)



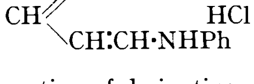
It was shown by Zincke and co-workers that the pyridine ring of 2 : 4-dinitrophenylpyridinium chloride (II) may be ruptured in a remarkable manner, giving 2 : 4-dinitroaniline and the enolic form of glutaconaldehyde (III). The latter compound was not isolated, but its formation was inferred from the preparation of derivatives, *e.g.*, glutaconaldehydedianilide hydrochloride (IV) (Zincke, *Annalen*, 1904, **330**, 361; Zincke, Heuser, and Möller, *ibid.*, 1904, **333**, 296; Zincke and Würker, *ibid.*, 1905, **338**, 107).

(III.)



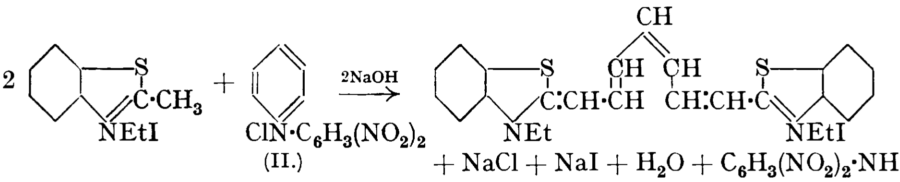
$$CH\left\langle\begin{matrix}CH\cdot CHO\\ CH{:}CH\cdot OH\end{matrix}\right.$$

(IV.)



$$CH\left\langle\begin{matrix}CH\cdot CH{:}NPh\\ CH{:}CH\cdot NHPh\end{matrix}\right. HCl$$

The first method of preparing tricarbocyanines consists in treating (II) with alkali, and presenting the resulting mixture of dinitroaniline and (III) with a heterocyclic ammonium salt containing a reactive methyl group; *e.g.*, the production of 2 : 2′-*diethylthiotricarbocyanine iodide* (V) from 1-methylbenzthiazole ethiodide may be represented thus :

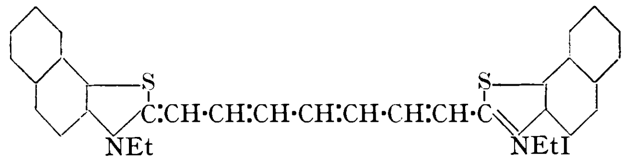

(V.)

The second method consists in condensing the ammonium salt with (IV). It was found, in general, best to effect the reactions in absolute-alcoholic solution by means of sodium ethoxide and the calculated quantities of the substances. The second method is markedly superior to the first, the yields of the purified dye (V) being 49% and 26% respectively : one reason for its superiority is that the organic by-product, aniline, is readily removable.

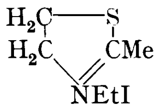
From the ethiodides of 1-methyl-α-naphthathiazole and 2-methyl-β-naphthathiazole, respectively, were prepared 2 : 2′-*diethyl*-5 : 6 : 5′ : 6′-*dibenzthiotricarbocyanine iodide* (VI) and 2 : 2′-*diethyl*-3 : 4 : 3′ : 4′-*dibenzthiotricarbocyanine iodide* (VII). Three other thiotricarbocyanines were also prepared.

Although 2 : 4-dimethylthiazole ethiodide forms a thiazolocarbocyanine (Fisher and Hamer, J., 1930, 2502), attempts to convert it into the thiazolotricarbocyanine were unsuccessful. On the other hand, 2-methylthiazoline ethiodide (VIII) smoothly gave 3 : 3′-*diethylthiazolinotricarbocyanine iodide*. From 1-methylbenzselenazole ethiodide (IX) was prepared 2 : 2′-*diethylselenotricarbocyanine iodide*. The corresponding dimethyl compounds were also prepared.

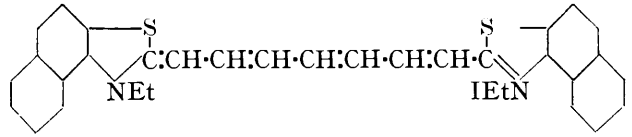
(VI.)



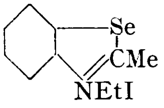
(VIII.)



(VII.)



(IX.)



1 : 1′-*Diethyl*-2 : 2′-*tricarbocyanine iodide* was prepared from quinaldine ethiodide, but its separation from the dyes which accompanied it was more difficult than with any of the preceding tricarbocyanines; the 2 : 2′-tricarbocyanine from *p*-toluquinaldine ethiodide was more easily obtained, but even here the yield of recrystallised dye was only 13%. With quaternary salts of lepidine and of 1-methylbenzoxazole, negative results were obtained.

Both methods of preparation gave negative results with 2 : 3 : 3-trimethylindolenine methiodide, but by modifying the second method so that this salt was heated with the dianilide (IV) in acetic anhydride solution, in the presence of sodium acetate, 1 : 3 : 3 : 1′ : 3′ : 3′-*hexamethylindotricarbocyanine iodide* (I) was obtained. This method differs in detail from that described by the other workers in this field.

In dealing with the tricarbocyanines, their instability to heat and light is manifest; it is perhaps responsible for the unsatisfactory analytical results obtained in some cases. It is illustrated also by the lowness of the melting points as compared with those of the carbocyanines. Thus with every one of nine pairs, the tricarbocyanine had the lower melting point; the average difference was 63°, the extremes being 21° and 103°.

For measurements of the absorption spectra of the dyes we are indebted to Messrs. A. L. Schoen, H. P. Cleveland, and L. A. Jones, of the Eastman Kodak Company. They used a Heele triple-prism spectrograph and examined methyl-alcoholic solutions. The dyes absorb light sharply, especially towards the red; there is no sign of the second absorption band which is characteristic of many cyanines. As would be expected, the absorption bands which lie furthest in the infra-red are those of the 2 : 2′-tricarbocyanines. The positions of the absorption maxima of ten tricarbocyanines have been compared with those recorded in the literature for the corresponding carbocyanines. The shift of the maximum towards the red end of the spectrum, on passing from carbocyanine to tricarbocyanine, is 190—205 $\mu\mu$. The seleno-series was at first supposed anomalous, but it appears that the absorption maxima recorded for the selenocarbocyanines require correction, and when this is made (Clark, this vol., p. 216) the supposed anomaly disappears.

It is well known that the cyanines, as a class, are photographic sensitisers, and that the position of the maximum of the band of extra-sensitivity, which any member may confer upon a photographic plate, corresponds, approximately, with that of the absorption maximum, being somewhat shifted towards the region of long wave-length. We began our study of the tricarbocyanines in the expectation that they, having longer polymethine chains than any other cyanine dyes, would make it feasible to photograph further into the infra-red than ever before. It is hoped to consider elsewhere the photographic aspect of the subject, but it may here be noted that this expectation has been fully realised.

EXPERIMENTAL.

2 : 4-Dinitrophenylpyridinium chloride (II) was obtained in almost colourless crystals (yield, 89%) by heating 2 : 4-dinitrochlorobenzene (100 g.) and pyridine (80 c.c.) at 100° for 15 min. (cf. Zincke, Heuser, and Möller, *loc. cit.*), the solid product being dissolved out with hot abs. EtOH (800 c.c.).

Glutaconaldehydedianilide hydrochloride (IV) was prepared by a modification of their method. The solid obtained from 2 : 4-dinitrophenylpyridinium chloride (80 g.) and aniline (80 c.c.) in hot spirit (160 c.c.) was collected when cold, and 2 : 4-dinitroaniline extracted from it by grinding with cold acetone (400 c.c. × 6). The residual red dye (77·3 g.; 96% yield) was dried to const. wt. in vac. at 60—80° and analysed by the method of Carius : this method of drying and analysis was used throughout this work, except where otherwise stated (Found : Cl, 12·4. Calc. for $C_{17}H_{17}N_2Cl$: Cl, 12·5%). The absorption maximum lies at λ 440 $\mu\mu$.

2 : 2′-*Diethylthiotricarbocyanine Iodide* (V).—2 : 4-Dinitrophenylpyridinium chloride (5 g.; 1 mol.), dissolved in hot abs. EtOH (50 c.c.), was treated with a solution of Na (0·82 g.; 2 atoms) in abs. EtOH (20 c.c.) and then immediately with one of 1-methylbenzthiazole ethiodide (10·84 g.; 2 mols.) in hot abs. EtOH (75 c.c.) : the mixture was boiled for 10 min. The *dye*, which crystallised, was washed with H_2O, and extracted in a Soxhlet apparatus, first with Et_2O (6·02 g. left), and then with acetone until the extract was pure blue. The yield of purified product was 26% (2·52 g.) (Found : I, 23·1%).

In the second, and better, method of prepn., boiling abs. EtOH (80 c.c.) containing glutaconaldehydedianilide hydrochloride (4 g.; 1 mol.) and 1-methylbenzthiazole ethiodide (8·56 g.; 2 mols.) was stirred while a solution of Na (0·65 g.; 2 atoms) in abs. EtOH (20 c.c.) was added and for 2 min. thereafter. The solid, when cold, was washed with H_2O and extracted with Et_2O. The residue (3·75 g.; 49% yield) was recrystallised from MeOH (2 l.); yield, 41% (Found : I, 23·3; S, 11·7. $C_{25}H_{25}N_2IS_2$ requires I, 23·3; S, 11·8%). The dye, m. p. 211° (decomp.), forms characteristic green crystals which give a blue methyl-alc. solution, with its maximum absorption at λ 765 $\mu\mu$.

It was similarly prepared by use of (a) glutaconaldehydedi-*p*-toluidide hydrochloride and (b) glutaconaldehydedi-β-naphthalide hydrochloride, the yields of washed product being 44% and 55%, respectively.

2 : 2′-*Dimethylthiotricarbocyanine chloride* was similarly prepared by treating glutaconaldehydedianilide hydrochloride (4 g.) and 1-methylbenzthiazole methochloride (7·03 g.) with Na in abs. alc. solution. The product was washed with H_2O, and extracted with Et_2O (residue, 2·52 g.; 34% yield) and then with acetone until a clean blue colour resulted. The undissolved dark green powder was dried for analysis at 80—100° (Found : Cl, 7·7; S, 14·3. $C_{23}H_{21}N_2ClS_2$ requires Cl, 8·35; S, 15·1%. $C_{23}H_{21}N_2ClS_2,\frac{1}{2}EtOH$ requires Cl, 7·9; S, 14·3%). M. p. 154° (decomp.). The dye has a well-defined absorption band with its crest at λ 760 $\mu\mu$.

2 : 2′-*Diethyl*-5 : 6 : 5′ : 6′-*dibenzthiotricarbocyanine Iodide* (VI).—Glutaconaldehydedianilide hydrochloride (8 g.; 1 mol.) and 1-methyl-α-naphthathiazole ethiodide (19·92 g.; 2 mols.) were boiled in abs. EtOH (160 c.c.) with a solution of Na (1·3 g.; 2 atoms) in abs. EtOH (40 c.c.) for 30 sec. The cold product was washed with H_2O, extracted with Et_2O, and boiled with MeOH

(300 c.c. × 3) until a blue-green filtrate resulted. The residue (5·64 g.; 31% yield) was dried in vac. at 90—110° (Found: I, 19·0; S, 10·1. $C_{33}H_{29}N_2IS_2$ requires I, 19·7; S, 9·95%. $C_{33}H_{29}N_2IS_2,\frac{1}{2}EtOH$ requires I, 19·0; S, 9·6%). After recrystn. from MeOH (550 c.c. per g.), the yield was 14% (Found: I, 19·2%). The dye is a bronze cryst. powder, m. p. 191° (decomp.); its max. absorption lies at λ 795 $\mu\mu$.

2 : 2′-*Dimethyl*-5 : 6 : 5′ : 6′-*dibenzthiotricarbocyanine chloride* was similarly prepared from glutaconaldehydedianilide hydrochloride (5 g.) and 1-methyl-α-naphthathiazole methochloride (8·77 g.). After being washed with H_2O and Et_2O, it was extracted with acetone until the extract was pure green: the residue (4·07 g.; 44% yield) was dried in vac. at 80—100° (Found: Cl, 6·6; S, 11·6. $C_{31}H_{25}N_2ClS_2$ requires Cl, 6·8; S, 12·2%). The almost black powder melted at 166° (decomp.). The sharply defined absorption band has its maximum at λ 785 $\mu\mu$.

2 : 2′-*Diethyl*-3 : 4 : 3′ : 4′-*dibenzthiotricarbocyanine iodide* (VII) was similarly prepared from glutaconaldehydedianilide hydrochloride (4 g.) and 2-methyl-β-naphthathiazole ethiodide (9·96 g.). After treatment with H_2O and with Et_2O, the product (4·88 g.; 54% yield) was boiled with insufficient MeOH to dissolve it all (100 c.c. × 8); the earlier filtrates were inky in colour, but the later ones were a pure blue-green, identical with the colour of a solution of the recryst. dye. The undissolved residue was obtained in 32% yield (2·85 g.) (Found: I, 19·2; S, 9·6. $C_{33}H_{29}N_2IS_2,\frac{1}{2}EtOH$ requires I, 19·0; S, 9·6%). The dye was only slightly sol. in hot MeOH (1½ l. per g.) and separated in a form from which the liquid filtered very slowly, the yield being reduced to 17% (Found: I, 19·2%). It existed as a dark powder before recrystn. and as green crystals afterwards. M. p. 183° (decomp.). The absorption maximum lies at λ 800 $\mu\mu$.

It was also prepared from 2 : 4-dinitrophenylpyridinium chloride (1·19 g.; 1 mol.) and 2-methyl-β-naphthathiazole ethiodide (3 g.; 2 mols.). After treatment with H_2O and Et_2O, fractional recrystn. of the residue (0·78 g.) from MeOH (20 c.c. × 5, and 50 c.c. × 3) was effected. From the last three fractions the total yield of the dye was 3% (0·10 g.). Its photographic action was identical with that of the specimen prepared by the other method.

2 : 2′-*Dimethyl*-3 : 4 : 3′ : 4′-*dibenzthiotricarbocyanine chloride* was prepared from glutaconaldehydedianilide hydrochloride (5 g.) and 2-methyl-β-naphthathiazole methochloride (8·77 g.). The residue left after H_2O and Et_2O extraction (4·49 g.; 49% yield) was extracted with acetone until the extract was green. The dark residual powder (37% yield; 3·36 g.) was dried in vac. at 80—100° (Found: Cl, 5·7; S, 11·6. $C_{31}H_{25}N_2ClS_2,EtOH$ requires Cl, 6·2; S, 11·2%). M. p. 181° (decomp.). The max. absorption occurs at λ 790 $\mu\mu$.

3 : 3′-*Diethylthiazolinotricarbocyanine Iodide*.—We are indebted to Dr. L. G. S. Brooker for a gift of 2-methylthiazoline, which he was the first to apply to cyanine dye formation (Kodak-Pathé, F.P. 718,471). Its ethiodide (4 g.) and glutaconaldehydedianilide hydrochloride (2·21 g.) were boiled in EtOH (20 c.c.) with Na (0·36 g.) in alc. solution (20 c.c.) for 90 sec. The resultant dye was washed with H_2O and extracted with Et_2O; the residue (1·27 g.; 36% yield), on recrystn. from MeOH (50 c.c.), gave 0·91 g. of characteristic grey crystals, m. p. 192° (decomp.), resembling metallic filings (Found: I, 28·2. $C_{17}H_{25}N_2IS_2$ requires I, 28·3%). Its alc. solution is deep blue, possessing a narrow absorption band with its maximum at λ 645 $\mu\mu$.

3 : 3′-*Dimethylthiazolinotricarbocyanine Iodide*.—2-Methylthiazoline methiodide (2 g.) was condensed with the dianilide in an exactly analogous manner. After the washing with H_2O and Et_2O, the product (1·09 g.; yield 32%) was boiled with MeOH (50 c.c.), and the residue recrystallised from MeOH (150 c.c.), whereby a 14% yield (0·49 g.) of steel-blue crystals, m. p. 213° (decomp.), resulted (Found: I, 30·1. $C_{15}H_{21}N_2IS_2$ requires I, 30·2%). Its absorption is almost identical with that of the preceding compound.

2 : 2′-*Diethylselenotricarbocyanine Iodide*.—1-Methylbenzselenazole has been obtained, in the laboratories of the Eastman Kodak Company, for the first time in almost colourless crystals, m. p. 32—33°. Its ethiodide (cf. Clark, J., 1928, 2313) (4·94 g.) was condensed with the dianilide hydrochloride just as was 1-methylbenzthiazole ethiodide, except that the time of heating was only 30 sec. The product (2·0 g.) was ground with small amounts of acetone (10 c.c. × 7) until the filtrate was a pure greenish-blue. The residue consisted of brilliant green crystals (1·50 g.; 34% yield). The method of determining I in the presence of Se has been recorded elsewhere (Hamer, *Analyst*, 1933, **58**, 26) (Found: I, 20·1. $C_{25}H_{25}N_2ISe_2$ requires I, 19·9%). After recrystn. from MeOH (1000 c.c. per g.), the yield was 17% (Found: I, 19·9%). M. p. 225° (decomp.). The blue solution shows a max. absorption at λ 770 $\mu\mu$.

2 : 2′-*Dimethylselenotricarbocyanine iodide* was similarly prepared from 1-methylbenzselenazole methiodide (11·9 g.). The dye was washed with H_2O and ground with cold acetone (100 c.c. × 5) until there was no further colour change. The residue (2·68 g.; 25% yield) was boiled

with MeOH (100 c.c. × 4). There remained a 21% yield (2·20 g.) of dark green solid, m. p. 198° (decomp.) (Found : I, 20·6. $C_{23}H_{21}N_2ISe_2$ requires I, 20·8%). The absorption maximum lies in the same position as that of the preceding diethyl compound.

6 : 6′-*Dimethyl*-1 : 1′-*diethyl*-2 : 2′-*tricarbocyanine Iodide*.—*p*-Toluquinaldine ethiodide (17·6 g.) was dissolved in boiling abs. EtOH (176 c.c.), and the dianilide (8 g.) added, followed by a solution of Na (1·3 g.) in abs. EtOH (40 c.c.). After boiling for 30 sec., the solution was allowed to cool; dye crystallised where the rod had scratched the sides of the beaker, and was filtered off, ground with H_2O, and extracted (6·92 g.) with Et_2O. The residue (6·11 g.) was boiled with MeOH (50 c.c., 100 c.c. × 2, 300 c.c. × 2); the crystals from the first three fractions were rejected, but the olive-green crystals from the last two (0·63 g.) consisted of *tricarbocyanine*. The bronze residue (1·87 g.; 12%) also consisted of tricarbocyanine (Found : I, 22·4. $C_{31}H_{33}N_2I$ requires I, 22·65%); part of it (1·64 g.) was recrystallised from MeOH (1000 c.c.), and bronze crystals resulted (1·25 g.), bringing the total yield of recryst. dye up to 13% (Found : I, 22·2%). M. p. 248° (decomp.). The green solution has an absorption maximum at λ 820 $\mu\mu$.

1 : 1′-*Diethyl*-2 : 2′-*tricarbocyanine Iodide*.—(1) This was similarly prepared from quinaldine ethiodide (8·4 g.). After the treatment with H_2O and Et_2O, the residue (1·52 g.) was ground with acetone (20 c.c. × 3) and then boiled with MeOH (20 c.c. × 4). After removal of a more sol. purple impurity, the green colour of the tricarbocyanine became manifest. The crystals from the last three fractions all gave a green spirit solution, but the total yield (0·16 g.), was only 2%.

(2) 2 : 4-Dinitrophenylpyridinium chloride (5 g.; 1 mol.), dissolved in hot abs. EtOH (50 c.c.), was treated with Na (0·82 g.; 2 atoms) in abs. EtOH (20 c.c.) and then with a hot abs. alc. solution (200 c.c.) of quinaldine ethiodide (10·62 g.; 2 mols.). The mixture was allowed to cool gradually. Next day the solid was washed with H_2O and extracted with Et_2O. The residue (5·06 g.) was ground with acetone (20 c.c., and 40 c.c. × 2), whereby much tar was removed, and boiled with MeOH (20 c.c. × 8), but the solution did not rapidly become pure green, as in the preceding method of prepn., and there was a small tarry residue. The bronze crystals obtained from the last four fractions (0·29 g.) amounted to a 4% yield (Found : I, 21·9. $C_{29}H_{29}N_2I$ requires I, 23·8%. $C_{29}H_{29}N_2I,MeOH$ requires I, 21·3%). M. p. 219° (decomp.); the olive-green crystals obtained by method (1) turned bronze at about 130°, but they too melted at 219°. The photographic action of the two samples is identical. The methyl-alc. solution possesses a broad absorption band with its crest at λ 810 $\mu\mu$.

1 : 3 : 3 : 1′ : 3′ : 3′-*Hexamethylindotricarbocyanine Iodide* (I).—To boiling Ac_2O (150 c.c.) were added 2 : 3 : 3-trimethylindolenine methiodide (5 g.; 2 mols.), glutaconaldehydedianilide hydrochloride (2·4 g.; 1 mol.), and anhyd. NaOAc (1·4 g.; 2 mols.). After boiling for 10 min., the hot deep-blue liquid was poured into H_2O (750 c.c.) containing KI (5 g.). The pptd. dye was removed and extracted with Et_2O. The residue (3·11 g.; 70% yield) was dissolved in hot MeOH (10 c.c.); from the filtered solution, bright green crystals (1·54 g.; 35% yield) separated on cooling. After recrystn. from MeOH (10 c.c.), the yield was 24% (Found : I, 23·35. $C_{29}H_{33}N_2I$ requires I, 23·7%). The crystals become bronze at about 160°; m. p. about 207° (decomp.). The max. absorption is at λ 740 $\mu\mu$.

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