

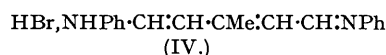
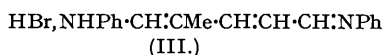
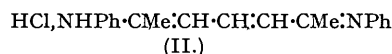
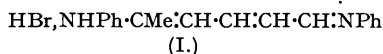
181. Symmetrical Tricarboyanines having One or More Methyl Groups as Substituents on the Chain.

By FRANCES M. HAMER and RUSSELL J. RATHBONE.

1-, 2-, and 3-Methyl derivatives of glutaconic aldehyde dianilide hydrohalide were prepared, also 1 : 5- and 1 : 3-dimethyl derivatives, from the appropriate pyridinium cyanobromides. They were condensed with heterocyclic quaternary salts to give tricarboyanines having β -, γ -, and δ -methyl groups, also $\beta\beta'$ - and $\beta\delta$ -dimethyl groups on the chain. Absorption maxima and photographic sensitising action of the dyes are recorded.

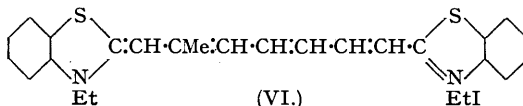
In a patent on photographic sensitising action, the four examples of chain-substituted tricarboyanines comprise one with a β -methyl and three with a δ -methyl group (I.G. Farbenind. A.-G., B.P. 394,537/1931). It is recorded that the intermediate for the first was prepared by König's method from β -naphthylamine, α -picoline, and cyanogen chloride in ether (*J. pr. Chem.*, 1904, **69**, 105), whilst that for the others was obtained analogously from aniline, γ -picoline, and cyanogen bromide. As no preparations whatever are described, we considered it desirable to record some.

Although König did originally describe the preparation of a dye from α -picoline, cyanogen chloride, and *o*-toluidine (*loc. cit.*), he subsequently disclaimed it but claimed that pure β -picoline does indeed form such a dye (*J. pr. Chem.*, 1904, **70**, 19). König and Schreckenbach (*ibid.*, 1913, **87**, 241) had found that 2 : 4-dinitrophenylpyridinium chloride does not, whilst pyridinium cyanobromide does, react with indoles to give dyes. α -Picoline and $\alpha\alpha'$ -lutidine do not combine with 1-chloro-2 : 4-dinitrobenzene to give pyridinium salts but we made them react with cyanogen bromide and thence, with aniline and hydrobromic or hydrochloric acid, obtained dyes (I) and (II). Similarly from β -picoline we prepared (III), referred to (but not described) by König (*ibid.*, 1904, **70**, 19), and from γ -picoline we prepared (IV). The product derived from γ -lutidine was used in condensations but we did not isolate a pure specimen of (V).



We compared the absorption maxima of (I)—(IV) in methyl-alcoholic solution with that of the parent dye having an unsubstituted chain. In passing from the parent dye to (II) and (III), there were bathochromic shifts of the maximum, of 45 \AA . and 10 \AA ., respectively, and hypsochromic shifts, of 90 \AA . and 65 \AA ., respectively, in passing to (I) and (IV). Whereas the parent dye is a photographic sensitiser, (I) was distinctly weaker, whilst (II), (III), and (IV) showed no sensitising power.

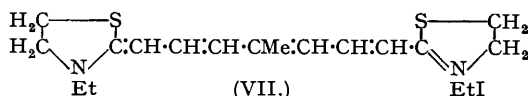
Glutaconic aldehyde dianilide hydrohalide condenses in the presence of sodium ethoxide, or of sodium acetate in acetic anhydride, with quaternary salts having reactive methyl groups to give tricarboyanines (Fisher and Hamer, *J.*, 1933, 189), but these condensing agents seemed unsuitable for use with the present substituted intermediates. However, Brooker had used piperidine at a low temperature (Kodak Ltd., B.P.P. 436,941/1933; 437,017/1933), and this method proved applicable here. By thus condensing 2-methylbenzthiazole ethiodide, with (I), (III), (IV), (II), and the crude (V), respectively, there resulted the β -methylthiatricboyanine (VI), which has been already described (I.G. Farbenind. A.-G., B.P. 394,537/1931), and



(VI.)

the corresponding γ - and δ -methyl-, and $\beta\beta'$ - and $\beta\delta$ -dimethyl-thiatricboyanines. By condensing 5 : 6-dimethoxy-2-methylbenzthiazole ethiodide and 2-methyl-6 : 7-benzthiazole ethiodide, respectively, with (II), the 5 : 6 : 5' : 6'-tetramethoxy- and 6 : 7 : 6' : 7'-dibenz-derivatives of the $\beta\beta'$ -dimethylthiatricboyanine were prepared. The dye obtained by condensing 2-methyl-6 : 7-benzthiazole ethiodide with (IV) has already been described (*idem, ibid.*). By condensing 2-methylbenzthiazole ethiodide with (II), (III), and (IV), respectively, there resulted a $\beta\beta'$ -dimethyl-, and a γ - and a δ -methyl-selenatricboyanine.

Condensation of (IV) and (V), respectively, with 2-methylthiazoline ethiodide gave the δ -methylthiazolinocarboyanine (VII) and the corresponding $\beta\delta$ -dimethyl compound.



We compared the absorption maxima in methyl-alcoholic solution of the chain-substituted tricarboyanines with the corresponding parent dyes: the figures are shown in the accompanying table. In one instance, introduction of a β -methyl group caused a bathochromic shift of 60 Å. Introduction of a γ -methyl group caused a bathochromic shift of 5 Å. and a hypsochromic shift

Chain.	Absorption (Å.) of tricarboyanine iodides:				
	Thia-.	Tetramethoxythia-.	Dibenzthia-.	Selena-.	Thiazolino-.
Unsubstituted	7620 *	8000	7970 *	7700 *	6450 †
β -Me	7680	—	—	—	—
γ -Me	7610	—	—	7705	—
δ -Me	7900	—	8250	8000	6750
$\beta\beta'$ -Me ₂	7720	7900	8290	7970	—
$\beta\delta$ -Me ₂	7060	—	—	—	6585

* Fisher and Hamer, *Proc. Roy. Soc.*, 1936, A, 154, 703.

† Fisher and Hamer, *J.*, 1933, 189.

of 10 Å. Introduction of a δ -methyl group had a more profound effect; thus, in four instances this caused consistently a bathochromic shift, the values being 280, 280, 300, and 300 Å. The introduction of $\beta\beta'$ -dimethyl groups caused a hypsochromic shift of 100 Å. in one case, but bathochromic shifts, of 100, 320, and 270 Å., respectively, in three others. $\beta\delta$ -Dimethyl groups produced a hypsochromic shift of 560 Å. and a bathochromic shift of 135 Å.

These chain-substituted tricarboyanines comprise photographic sensitizers but, as already noted for symmetrical dicarboyanines carrying a methyl group on the chain (Hamer and Rathbone, *J.*, 1945, 595), it cannot be said that they are in general better than the parent dyes with an unsubstituted chain.

EXPERIMENTAL.

1-Anilino-5-anilo-1-methyl-1:3-pentadiene Hydrobromide (I).—Cyanogen bromide (5 g.; 1 mol.) was added to water (30 c.c.) which was cooled with ice. Aniline (10 c.c.; >2 mols.) was added and α -picoline (5 c.c.; 1 mol.) was gradually stirred in. After 30 minutes in ice, the mixture was gradually treated with ice-cold hydrobromic acid (14 c.c., *d* 1.45; 2.5 mols.). After standing in the cold overnight, the red solid was filtered off and ground once with water (20 c.c.) and thrice with acetone (19% yield; 3.00 g.). This and the other pentadiene derivatives were dried in a vacuum desiccator before analysis (Found: Br, 23.25. C₁₈H₁₉N₂Br requires Br, 23.3%). The maroon crystals had m. p. about 155° (decomp.), depending on the rate of heating. Their absorption maximum was at 4760 Å. whereas the corresponding substance with an unsubstituted chain had its maximum at 4870 Å. They sensitised a gelatino-bromide photographic emulsion weakly up to 5700 Å.

1-Anilino-5-anilo-1:5-dimethyl-1:3-pentadiene hydrochloride (II) was similarly prepared from aniline (10 c.c.), cyanogen bromide in ice-cold water, and $\alpha\gamma$ -lutidine, followed by concentrated hydrochloric acid. The solid was filtered off, ground with water (40 c.c.) and thrice with acetone (40 c.c. \times 2, 60 c.c.). The yield (7.28 g.) was 25% (Found: Cl, 11.3. C₁₈H₂₁N₂Cl requires Cl, 11.3%). The red crystals had m. p. 150—151° (decomp.). The absorption maximum was at 4915 Å. and the dye had no photographic sensitising action.

1-Anilino-5-anilo-2-methyl-1:3-pentadiene hydrobromide (III) was similarly prepared from cyanogen bromide (5 g.) in cold water with aniline and β -picoline, followed by hydrobromic acid. The yield of washed hydrobromide was 37% (Found: Br, 22.8. C₁₈H₁₉N₂Br requires Br, 23.3%). The maroon crystals had m. p. about 148° but dependent on the rate of heating. The absorption maximum was at 4880 Å. The dye did not sensitise. In another experiment more hydrobromic acid (another 2.5 mols.) was added and produced a pale pink solid. It was filtered off and washed with acetone (2.4 g. obtained; 9% yield) and appeared to be the dihydrobromide, m. p. 239° (decomp.) (Found: Br, 37.75. C₁₈H₂₀N₂Br₂ requires Br, 37.7%). The hydrochloride was similarly prepared.

1-Anilino-5-anilo-3-methyl-1:3-pentadiene Hydrobromide (IV).—To cyanogen bromide (5 g.; 1 mol.) in water (10 c.c.), with slight cooling, was added a mixture of γ -picoline (5 c.c.; 1 mol.) and aniline (10 c.c.; >2 mols.). A vigorous reaction occurred with rise of temperature. Hydrobromic acid was stirred in (14 c.c., *d* 1.45; 2.5 mols.), followed quickly by ice-water. The yield of washed solid was 6.65 g. (31%), and this was used in condensations. On recrystallising a sample from methyl alcohol (50 c.c. per g.) the yield was 13% (Found: Br, 23.2. C₁₈H₁₉N₂Br requires Br, 23.3%). The dark maroon crystals had m. p. 167° (decomp.). The absorption maximum was at 4805 Å. and there was no photographic sensitisation. When the reaction temperature was kept down by cooling with ice, the yield of dye was only 1%.

1-Anilino-5-anilo-1:3-dimethyl-1:3-pentadiene Hydrobromide (V).—A solution of aniline (10 c.c.; 2.2 mols.) and $\alpha\gamma$ -lutidine (5 c.c.; 1 mol.) in ether (20 c.c.) was added to a solution of cyanogen bromide

(5 g.; 1 mol.) in ether (10 c.c.), and the mixture warmed for 2 minutes. Hydrobromic acid (14 c.c., d 1.45; 2.5 mols.) was added. The ether-washed solid was obtained in 51% yield (8.08 g.), but tended to become oily on standing in the air. It was used as quickly as possible for dye condensations, being kept meanwhile in a vacuum desiccator.

Bis-2-(3-ethylbenzthiazole)- β -methylheptamethincyanine Iodide (VI).—2-Methylbenzthiazole ethiodide (3.05 g.; 2 mols.) and 1-anilino-5-anilo-1-methyl-1:3-pentadiene hydrobromide (I) (1.72 g.; 1 mol.) were added to ice-cold absolute alcohol (30 c.c.), and a cooled solution of piperidine (1.1 c.c.; 2.2 mols.) in alcohol (5 c.c.) was stirred in. After three days in the ice-chest, the solid was filtered off, washed with alcohol and with ether, and finally with warm water (40 c.c.), after which the yield was 65% (1.84 g.). After recrystallisation from methyl alcohol (650 c.c.), the yield was 33% (0.96 g.) and, after a second recrystallisation (450 c.c. per g.) in the presence of charcoal (0.75 g. per g.), it was 10%. For analysis it was dried to constant weight in a vacuum at 60–80° and this method of drying was applied to the subsequent dyes also (Found: I, 22.6. Calc. for $C_{28}H_{27}N_2IS_2$: I, 22.75%). The green crystals with a golden reflex had m. p. 215° (decomp.) (see B.P. 394,537/1931, example 6).

Bis-2-(3-ethylbenzthiazole)- γ -methylheptamethincyanine Iodide.—A similar preparation was carried out but with (III). The crude product (60% yield) was recrystallised from methyl alcohol (42 c.c. per g.), and gave dark green crystals, in 16% yield (Found: I, 22.8. $C_{27}H_{27}N_2IS_2$ requires I, 22.7%); m. p. 166° (decomp.). The sensitising maximum was at 8150 Å.

Bis-2-(3-ethylbenzthiazole)- δ -methylheptamethincyanine iodide was similarly prepared but with (IV). The crude dye (76% yield) was recrystallised from methyl alcohol (425 c.c. per g.) and gave a 43% yield of light green crystals with a gold reflex (Found: I, 22.8. $C_{28}H_{27}N_2IS_2$ requires I, 22.75%); m. p. 206° (decomp.). Sensitisation extended from 7000 to 9000 Å. with the maximum at 8300.

Bis-2-(3-ethylbenzthiazole)- $\beta\beta'$ -dimethylheptamethincyanine iodide was similarly prepared from 2-methylbenzthiazole ethiodide (2.94 g.) and (II). The product was ground with water (20 c.c.), and twice with acetone (20 c.c. \times 2), boiled out twice with methyl alcohol (50 c.c. \times 2), and recrystallised from methyl alcohol (1350 c.c.), the yield of green crystals then being 10% (0.27 g.) (Found: I, 22.5. $C_{27}H_{29}N_2IS_2$ requires I, 22.2%); m. p. 208° (decomp.). The sensitising maximum was at 8350 Å.

Bis-2-(3-ethylbenzthiazole)- $\beta\delta$ -dimethylheptamethincyanine Iodide.—Starting from 2-methylbenzthiazole ethiodide (12.2 g.) and crude (V), the crude yield was only 2% (0.2 g.). After boiling out with absolute alcohol (5 c.c.) and recrystallisation from methyl alcohol (15 c.c.), it was less than 1% (0.08 g.) [Found (micro-analysis by Weiler and Strauss): I, 22.6. $C_{27}H_{29}N_2IS_2$ requires I, 22.2%]. The bright green crystals had m. p. 155° (decomp.). Photographic sensitisation was from 7200 to 8500 with the maximum at 8200 Å.

Bis-2-(5:6-dimethoxy-3-ethylbenzthiazole)- $\beta\beta'$ -dimethylheptamethincyanine Iodide.—5:6-Dimethoxy-2-methylbenzthiazole ethiodide (5.84 g.; 2 mols.), (II) (2.5 g.; 1 mol.), and absolute alcohol (40 c.c.) were stirred mechanically at 80°. A solution of piperidine (1.8 c.c.; 2.2 mols.) in alcohol (up to 12 c.c.) was added in 12 portions (1 c.c. per minute) and stirring was for 12 minutes. After cooling, the solid was filtered off, washed once with alcohol, twice with warm water (20 c.c. \times 2), and repeatedly with acetone. The residue (0.27 g.; 5% yield) was recrystallised from methyl alcohol (500 c.c.), and the yield was 2% (Found: I, 18.3. $C_{31}H_{37}O_4N_2IS_2$ requires I, 18.3%). The green crystals had m. p. 210° (decomp.).

Bis-2-(3-ethyl-6:7-benzbenzthiazole)- $\beta\beta'$ -dimethylheptamethincyanine Iodide.—This was prepared from 2-methylbenzthiazole ethiodide (6.82 g.) and (II), with piperidine in ice-cold alcohol. The washed solid was boiled out with methyl alcohol (100 c.c.) and recrystallised from it (1000 c.c.), being obtained in 8% yield (0.51 g.) (Found: I, 19.2. $C_{35}H_{33}N_2IS_2$ requires I, 18.9%). The bronze crystals had m. p. 187° (decomp.). The sensitising maximum was at 8800 Å. In the corresponding preparation carried out with 2-methyl-4:5-benzbenzthiazole ethiodide, the yield of tricarbocyanine was only 1%.

Bis-2-(3-ethyl-6:7-benzbenzthiazole)- δ -methylheptamethincyanine Iodide.—This was similarly prepared from 2-methyl-6:7-benzbenzthiazole ethiodide (3.55 g.) and (IV). The washed solid (1.02 g.) was boiled out with methyl alcohol (20 c.c.) and recrystallised from it (1100 c.c.). An 18% yield (0.6 g.) was obtained (Found: I, 19.15. Calc. for $C_{34}H_{31}N_2IS_2$: I, 19.3%). The bronze crystals had m. p. 187° (decomp.) (see B.P. 394,537/1931, example 8).

Bis-2-(3-ethylbenzselazole)- $\beta\beta'$ -dimethylheptamethincyanine Iodide.—2-Methylbenzselazole ethiodide (5.63 g.) was similarly allowed to react with (II). The washed solid was boiled out with methyl alcohol (70 c.c.), and recrystallised from it (1750 c.c.). The yield (0.97 g.) was 18% (Found: I, 19.3. $C_{27}H_{29}N_2IS_2$ requires I, 19.4%). The green crystals had m. p. 214–217° (decomp.), the exact temperature depending on the rate of heating. The sensitising maximum was at 8450 Å.

Bis-2-(3-ethylbenzselazole)- γ -methylheptamethincyanine iodide was similarly prepared from 2-methylbenzselazole ethiodide (7.71 g.) and (III). The washed product (3.17 g.) was boiled out with methyl alcohol (60 c.c.) and recrystallised from it (1000 c.c.), the yield being 18% (1.26 g.) (Found: I, 19.5. $C_{26}H_{27}N_2IS_2$ requires I, 19.45%). The green crystals melted at 214° (decomp.). The sensitising maximum was at 8350 Å.

Bis-2-(3-ethylbenzselazole)- δ -methylheptamethincyanine iodide was similarly prepared from 2-methylbenzselazole ethiodide (3.52 g.) and (IV). The washed solid (1.65 g.) was boiled out with methyl alcohol (30 c.c.) and recrystallised from it (1400 c.c.), being obtained in 30% yield (0.96 g.) (Found: I, 19.65. $C_{26}H_{27}N_2IS_2$ requires I, 19.5%). It formed light green crystals with a golden reflex; m. p. 213° (decomp.). Sensitisation was from 7000 to 9000 Å. with a maximum at 8400.

Bis-2-(3-ethyl- Δ^2 -thiazoline)- δ -methylheptamethincyanine Iodide (VII).—This was prepared from 2-methylthiazoline ethiodide (5.14 g.) and (IV). The washed dye (3.85 g.) was recrystallised from methyl alcohol (25 c.c.), and the yield was 59% (2.65 g.) (Found: I, 27.5. $C_{18}H_{17}N_2IS_2$ requires I, 27.45%). It formed bluish-black crystals with a metallic lustre; m. p. 134° (decomp.). Sensitisation was from 6100 to 7500 Å., with the maximum at 7100.

Bis-2-(3-ethyl- Δ^2 -thiazoline)- $\beta\delta$ -dimethylheptamethincyanine Iodide.—In a similar preparation carried out with (V), the yield of washed dye was only 5% and after recrystallisation from methyl alcohol (40 c.c. per g.) was 2% [Found (micro-analysis by Weiler and Strauss): I, 26.8. $C_{18}H_{19}N_2IS_2$ requires

I, 26.65%]. The bluish-grey crystals had m. p. 165° (decomp.). The dye sensitised from 6000 to 7300 with the maximum at 6900 Å.

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