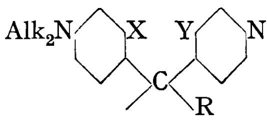
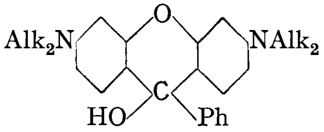
400. *The Synthesis and Properties of 2 : 7-Tetramethyldiaminoanthraquinone, 2 : 7-Tetramethyldiamino-10-hydroxy-10-phenylanthrone, and Related Compounds.*

By D. C. Rhys Jones and Frederick A. Mason.

Many important types of dyes, mainly of basic character, such as those of the diphenylmethane, triphenylmethane, acridine, pyronine, thiopyronine, thioxanthen, and rhodamine series, contain the typical skeleton $Alk_2N\cdot C_6H_4\text{-}\overset{|}{\underset{|}{C}}\text{-}C_6H_4\cdot NAlk_2$ and may be regarded as derived from parent substances of the general type (I), where R = hydrogen or an aryl radical, X and Y = hydrogen atoms or –O–, –S–, –NH–, etc. (as, for instance, a pyronine of formula II). In the case of many of the triphenylmethane dyes these are, of course, readily made by condensing Michler's ketone (4 : 4′-tetramethyldiaminobenzophenone) with suitable components.



(I.)



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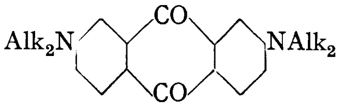
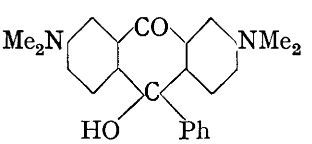
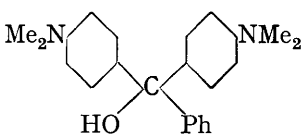


(III.)

A 2 : 7-tetra-alkyldiaminoanthraquinone (III) can be regarded as a substituted Michler's ketone and accordingly might be expected to condense with suitable aromatic components to yield carbinol bases of the type (IV) (where X and Y of formula I = –CO–), analogous in structure with those of the well-known triphenylmethane type (V) :



(IV.)



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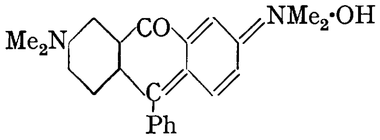

(VI.)

Substances of the type (III) have now been prepared, their properties examined, and basic dyes derived from carbinols of type (IV) have been synthesised, though with some difficulty.

The substance (III; Alk = Me) was prepared by the action of dimethylamine upon 2 : 7-dichloroanthraquinone in presence of a suitable solvent for the very sparingly soluble, and relatively inactive, dichloroanthraquinone, the preparation of which in quantity also called for detailed investigation.

In preliminary experiments with aqueous dimethylamine, anthraquinone-2 : 7-disulphonic acid was recovered unchanged after 40 hours' heating at 220°, 2-chloroanthraquinone-7-sulphonic acid yielded only 2-dimethylaminoanthraquinone-7-sulphonic acid, and 2 : 7-dichloroanthraquinone gave 2-*chloro*-7-*dimethylaminoanthraquinone* after prolonged heating under pressure. As it was thought that the difficulty of replacing the second chlorine atom might be due to the insolubility of the anthraquinone derivatives, experiments were carried out with amyl alcohol, pyridine, and anisole as solvents, with successful results, the desired 2 : 7-*tetramethyldiaminoanthraquinone* being obtained.

2 : 7-Tetramethyldiaminoanthraquinone was not attacked by sodium amalgam in amyl alcohol or by zinc dust and ammonia. Reduction with zinc dust and hydrochloric acid or, better, tin and hydrochloric acid in glacial acetic acid solution produced 2 : 7-*tetramethyldiamino*-9(or 10)-*anthrone*, which formed an acetyl derivative and was oxidised by ferric chloride to the *dianthrone*.

The general behaviour of 2 : 7-tetramethyldiaminoanthraquinone indicated that the introduction of a carbonyl group connecting the two ortho-positions in 4 : 4′-tetramethyldiaminobenzophenone had considerably inhibited the reactivity of the carbonyl group already present, and accordingly it was found that all attempts to prepare a dye of formula (IV) by direct condensation of the anthraquinone compound with suitable components (such as dimethylaniline) in presence of phosphoryl chloride in the known manner, yielded no results, the basic components being recovered unchanged even after prolonged heating; the corresponding anthrone also proved to be an intractable substance.

A dye of the desired structure was finally synthesised by two independent methods: (*a*) From the reaction between phenylmagnesium bromide and 2 : 7-tetramethyldiaminoanthraquinone in ethereal suspension, 2 : 7-*tetramethyldiamino*-10-*hydroxy*-10-*phenylanthrone* (IV) was finally isolated (compare Clarke, *Ber.*, 1908, **41**, 935; Haller and Guyot, *Compt. rend.*, 1904, **138**, 327; Barnett and Cook, J., 1927, 1724).

(*b*) Rodd and Lynch have shown (E.P. 272,321, 301,193; J., 1927, 2174, 2179) that 4 : 4′-tetramethyldiaminobenzophenone reacts with chlorobenzene in boiling toluene solution in presence of metallic sodium to yield malachite-green, presumably with the intermediate formation of the compound $(Me_2N{\cdot}C_6H_4)_2C(ONa)Na$. A similar experiment with 2 : 7-tetramethyldiaminoanthraquinone in place of the substituted benzophenone afforded a green dye identical with that obtained by the Grignard synthesis. The Rodd–Lynch sodium synthesis has not hitherto been applied to the anthraquinone series.

The analogous tolyl, anisyl, and naphthyl derivatives were also prepared by both methods; all three formed green salts of similar shade, the naphthyl being the deepest; the difference in colour was not so marked as in the corresponding triphenylmethane dyes. The methyl derivative was also prepared, but was not obtained pure. Attempts to prepare the analogue of crystal-violet from 2 : 7-tetramethyldiaminoanthraquinone by either method were unsuccessful.

EXPERIMENTAL.

2 : 7-*Dichloroanthraquinone.*—Anthraquinone-2 : 7-disulphonic acid was boiled for 10 hours with excess of potassium chlorate in dilute hydrochloric acid (compare Schmidt, *J. pr. Chem.*, 1874, **9**, 266; Fr. Bayer & Co., G.P. 205,195, 205,913); a mixture of 2-chloroanthraquinone-7-sulphonic acid and about 10% of the dichloro-compound separated. This mixture was again treated with potassium chlorate and dilute hydrochloric acid, the yield of the dichloro-compound being raised to 30—40%. The mixture of 2 : 7-dichloro- and 2-chloro-7-sulpho-anthraquinone (20 g.) was extracted twice with boiling carbon tetrachloride (400 c.c.); the filtrates deposited 6·1 g. of the pure dichloro-compound.

2 : 6-Dichloroanthraquinone was produced in a similar manner from the 2 : 6-disulphonic acid (yield, 30—40%).

2-Chloroanthraquinone-7-sulphonic acid (5 g.), heated with phosphorus pentachloride (4 g.) in phosphoryl chloride suspension, gave 2-*chloroanthraquinone*-7-*sulphonyl chloride*, which formed yellow crystals, m. p. 205°, from benzene (Found : S, 9·2; Cl, 20·5. $C_{14}H_6O_4Cl_2S$ requires S, 9·4; Cl, 20·8%). On distillation under 20 mm. pressure the sulphonyl chloride (4 g.) melted and sublimed, but finally pure 2 : 7-dichloroanthraquinone (0·7 g.) distilled.

2-*Dimethylaminoanthraquinone*-7-*sulphonic Acid.*—2-Chloroanthraquinone-7-sulphonic acid (4 g.) was heated with 33% aqueous dimethylamine (20 c.c.) at 185—190° for 8 hours. The product was salted out with sodium chloride (3·8 g.) and crystallised from saturated brine, forming fine purple needles (Found : C, 53·8; H, 3·2; N, 4·0; S, 8·6. $C_{16}H_{12}O_5NSNa$ requires C, 54·4; H, 3·4; N, 4·0; S, 9·0%).

The acid, obtained by evaporating a concentrated aqueous solution of the *sodium* salt and the theoretical quantity of concentrated hydrochloric acid and extracting the residue with hot absolute alcohol, formed deep purple crystals, very readily soluble in water. When dry hydrogen chloride was passed through a solution of the sodium salt (6 g.) in glacial acetic acid (30 c.c.), the *monohydrochloride* separated as colourless needles (2 g.), soluble in water to a deep purple solution (Found : Cl, 10·1. $C_{16}H_{13}O_5NS,HCl$ requires Cl, 9·7%).

2-Dimethylaminoanthraquinone-6-sulphonic acid was prepared from 2-chloroanthraquinone-6-sulphonic acid and dimethylamine in the same way as for the 2 : 7-compound and had closely similar properties, the *sodium* salt affording deep purple solutions (Found : N, 4·2; S, 8·5%).

2-Diethylaminoanthraquinone-7-sulphonic acid, obtained similarly, was a deep purple substance closely resembling its analogues, as also does its *sodium* salt (Found : N, 3·6; S, 8·0. $C_{18}H_{16}O_5NSNa$ requires N, 3·7; S, 8·4%).

2-*Chloro*-7-*dimethylaminoanthraquinone.*—2 : 7-Dichloroanthraquinone (4 g.) was heated with

33% aqueous dimethylamine (16 c.c.) and copper powder (0·2 g.) for 8 hours at 180°. The *product* crystallised from amyl alcohol in scarlet needles (2·8 g.), m. p. 256° (Found : C, 66·7; H, 4·3; N, 5·0; Cl, 12·2. $C_{16}H_{12}O_2NCl$ requires C, 67·2; H, 4·2; N, 4·9; Cl, 12·4%), sparingly soluble in methyl and ethyl alcohol and easily soluble in hot amyl alcohol, benzene, toluene, and chloroform. Its yellow solution in concentrated sulphuric acid deposited the unchanged base on dilution with water; it also formed with concentrated hydrochloric acid a colourless insoluble hydrochloride, hydrolysed immediately by water. With alkaline sodium hydrosulphite it formed an orange vat which had no affinity for cotton.

2-*Chloro*-7-*diethylaminoanthraquinone*, prepared in a similar manner from 2 : 7-dichloroanthraquinone (4 g.) and diethylamine (4 g.) in water (15 c.c.), had m. p. 254°, and properties almost identical with those of the dimethylamino-derivative (Found : Cl, 11·0. $C_{18}H_{16}O_2NCl$ requires Cl, 11·3%).

2-*Chloro*-6-*dimethylaminoanthraquinone*, m. p. 258°, was slightly paler in colour than the 2 : 7-compound, but otherwise had almost identical properties (Found : Cl, 12·1%).

2 : 7-*Tetramethyldiaminoanthraquinone*.—2 : 7-Dichloroanthraquinone (5 g.), 50% aqueous dimethylamine (16 c.c.), amyl alcohol (20 c.c.), and copper powder (0·2 g.) were heated in a sealed tube at 220° for 8 hours. The product consisted of a magma of deep ruby-red platelets in a deep red-brown amyl-alcoholic solution, together with a pale green aqueous layer (yield, 3·3 g.; a further 0·4 g. was recovered from the amyl-alcoholic solution). The crude 2 : 7-*tetramethyldiaminoanthraquinone*, after successive recrystallisations from amyl alcohol, chloroform, and pyridine or toluene, formed ruby-red platelets, m. p. 317° (Found : C, 72·8, 73·0; H, 6·2, 6·4; N, 9·2. $C_{18}H_{18}O_2N_2$ requires C, 73·5; H, 6·1; N, 9·5%).

The use of an amyl-alcoholic solution of dimethylamine gave similar results, but the presence of water did not appear to have any adverse effect. Larger-scale preparations (up to 40 g. of dichloroanthraquinone) in an autoclave holding a porcelain beaker gave yields of 50—60% of the theoretical.

The pure substance was only sparingly soluble in methyl or ethyl alcohol, more soluble in tetrachloroethane, nitrobenzene, pyridine, glacial acetic acid, and amyl alcohol. The finely powdered substance dissolved in boiling chloroform, from which it crystallised in red needles containing $2CHCl_3$, which disappeared rapidly on exposure to air, leaving a scarlet powder of the original substance. In concentrated sulphuric acid 2 : 7-tetramethyldiaminoanthraquinone formed a yellow solution, which on cautious dilution with ice turned bluish-red and then deposited a red precipitate of the base. The solution in concentrated hydrochloric acid behaved in a similar manner. A suspension of the base in water dyed acetate silk in salmon-pink shades, but the orange hydrosulphite vat showed no affinity for cotton. The absorption curve in glacial acetic acid solution showed a maximum at λ 470 $\mu\mu$ and one absorption band at λ 520 $\mu\mu$.

2 : 7-*Tetraethyldiaminoanthraquinone*, m. p. 285°, closely resembled the tetramethyl analogue in appearance and properties (Found : N, 8·1. $C_{22}H_{26}O_2N_2$ requires N, 8·0%).

2 : 6-*Tetramethyldiaminoanthraquinone* formed dark red needles, m. p. 289°, from amyl alcohol or pyridine (Found : N, 9·5%). It was very much more soluble in organic solvents than the 2 : 7-isomeride and for this reason it was unnecessary to effect any very special purification of the anthraquinone-2 : 7-disulphonic acid, which might contain small amounts of the 2 : 6-isomeride.

Monobromo-2 : 7-*tetramethyldiaminoanthraquinone*.—Bromination of the base (2·0 g.) in glacial acetic acid (500 c.c.) with bromine (2·2 g.) at room temperature afforded an orange-brown crystalline deposit (1·2 g.); a further amount (1·5 g.) was obtained on dilution with water. The *bromo*-compound formed orange-red needles from amyl alcohol, m. p. 234° (Found : N, 7·5; Br, 20·9. $C_{18}H_{17}O_2N_2Br$ requires N, 7·5; Br, 21·4%).

Nitration of 2 : 7-*Tetramethyldiaminoanthraquinone*.—The base (3 g.) in concentrated sulphuric acid (30 c.c.), treated with 0·6 c.c. of concentrated nitric acid in 10 c.c. of sulphuric acid and diluted, gave a mixture of isomeric mononitro-derivatives, m. p. 260—282° after crystallisation from amyl alcohol (Found : N, 12·9. $C_{18}H_{17}O_4N_3$ requires N, 12·4%). When a solution of 2 : 7-tetramethyldiaminoanthraquinone in 50% nitric acid was warmed, an orange-red nitro-compound separated, m. p. 264° after crystallisation from amyl alcohol.

Reduction of 2 : 7-*Tetramethyldiaminoanthraquinone*.—(i) Reduction with aluminium or copper powder in concentrated sulphuric acid, followed by dilution with water and extraction with ether, afforded a thick yellow oil, which readily re-oxidised to the original base on exposure to the air.

(ii) Reduction with concentrated hydrochloric acid and stannous chloride afforded a yellow crystallisable product.

(iii) The same product was obtained more conveniently thus : 2 : 7-tetramethyldiaminoanthraquinone (4 g.) and granulated tin (6 g.) were added to glacial acetic acid (80 c.c.). The liquid was boiled under reflux while concentrated hydrochloric acid was dropped in slowly, the colour of the solution changing from deep orange-red to pale yellowish-orange during 1 hour. The liquid was diluted to 250 c.c., and excess of sodium acetate added. The yellow precipitate obtained was quickly dried in a vacuum (yield, 3·2 g.). It crystallised in yellow platelets from alcohol and in needles from chloroform, both forms melting at 180° (Found : N, 9·7. $C_{18}H_{20}ON_2$ requires N, 10·0%). The substance was presumably 2 : 7-*tetramethyldiamino*-9(or 10)-*anthrone*; it was fairly easily soluble in organic solvents, afforded pale yellow solutions in dilute mineral acids, and was sparingly soluble in hot aqueous alkalis. An ethereal or alcoholic solution gradually deposited orange-red crystals of the parent base on exposure to the air.

Acetylation of the anthrone. The reduction product (from 2 g. of 2 : 7-tetramethyldiaminoanthraquinone) was boiled with anhydrous sodium acetate (0·5 g.), acetic anhydride (60 c.c.), and pyridine (5 c.c.) for 15 minutes. On cooling and dilution a precipitate was obtained (2·2 g.), which formed orange needles, m. p. 173°, from alcohol.

Oxidation of the anthrone. The crude anthrone (4 g.) was dissolved in boiling glacial acetic acid (200 c.c.) and boiled for 4 hours with a concentrated aqueous solution of ferric chloride (4 g.). On dilution with water a brown precipitate was obtained, from which unchanged base was extracted with dilute hydrochloric acid (10 c.c.). The green filtrate was neutralised with alkali, and the resultant green precipitate extracted with chloroform, which on evaporation yielded 0·3 g. of yellowish-green needles, m. p. 330°. The same substance was also obtained on boiling 2 : 7-tetramethyldiaminoanthraquinone in chloroform or tetrachloroethane solution for some time, and from its general properties it was assumed to be 2 : 7 : 2′ : 7′-*octamethyltetra-amino*-9(10) : 9′(10′)-*dianthrone* (Found : C, 77·9; H, 6·7; N, 9·8. $C_{36}H_{36}O_2N_4$ requires C, 77·7; H, 6·5; N, 10·0%).

2 : 7-*Tetramethyldiamino*-10-*hydroxy*-10-*phenylanthrone*.—(*Method a*) Finely powdered 2 : 7-tetramethyldiaminoanthraquinone (3 g.) was added to the solution of phenylmagnesium bromide prepared from bromobenzene (6 g.), magnesium (2 g.), and ether (200 c.c.). Reaction occurred immediately with production of a brown solution, which was boiled for 3 hours. After cooling, the mixture of brown solution and dark brown powder was decomposed by the addition of ice and ammonium chloride solution; the product (yellow ethereal layer, deep green aqueous layer, and a deep green solid), on addition of dilute hydrochloric acid, afforded a deep green acid solution and a colourless ethereal layer. The acid solution was filtered from unchanged 2 : 7-tetramethyldiaminoanthraquinone (1·8 g.) and neutralised with sodium hydroxide, with formation of a dark green precipitate of the colour base (VI), which on warming, or on further treatment with alkali, was isomerised into the yellow *carbinol* base (IV) (yield, 1·4 g.). The base was extracted from the associated magnesium hydroxide by means of ether, and the solvent evaporated. The resultant yellow oil crystallised in small nodules, m. p. 273°, from ether–light petroleum (Found : C, 76·9; H, 6·2; N, 7·8. $C_{24}H_{24}O_2N_2$ requires C, 77·4; H, 6·4; N, 7·5%).

The yellow crystals dissolved readily in dilute hydrochloric acid, giving a faintly green solution which gradually became deep green. In concentrated hydrochloric acid the solution was deep yellow. From the green solution in dilute hydrochloric acid, wool, silk, and tannin-mordanted cotton were dyed in bright green shades fast to acids, alkalis, and washing; the colour was, however, fugitive to light, a rough comparison indicating that it was only very slightly faster than malachite-green in this respect. The *zincichloride*, precipitated on addition of a concentrated aqueous solution of zinc chloride to a solution of the hydrochloride of the dye, crystallised from water as microscopic, dark green crystals (Found: Zn, 11·9. $C_{24}H_{23}ON_2Cl,ZnCl_2$, requires Zn, 12·4%).

Absorption spectrum. The chief absorption band of a solution of the hydrochloride in water was at λ 650 μμ. There was also a strong absorption at about λ 450 μμ.

(*Method b*) 2 : 7-Tetramethyldiaminoanthraquinone (3 g.), sodium (2 g.), chlorobenzene (2 g.), and toluene (200 c.c.) were boiled together under reflux for 4 hours, forming a brownish-red solution and a brown powder. The liquid was cooled, the unchanged sodium removed, and the residue shaken out with dilute hydrochloric acid. On warming, a deep green solution was obtained, from which 2 : 7-tetramethyldiamino-10-hydroxy-10-phenylanthrone was isolated as described in method *a*.

Antiseptic properties. In view of the known antiseptic properties of dyes of the triphenylmethane series a comparative test was carried out on " Chapman's Bacterium " (*J. Inst. Brewing*, **1925**, **31**, 13), thymol being used as a standard; 0·01 g. of tetramethyldiamino-10-hydroxy-10-phenylanthrone in 10 c.c. of a sterile gelatin medium was just sufficient to inhibit growth, the inhibiting dose of thymol under the same conditions being 0·1 g.

2 : 7-*Tetramethyldiamino*-9(10)-*hydroxy*-9(10)-*phenyldihydroanthracene*.—2 : 7-Tetramethyldiamino-9(10)-anthrone (1 g.) was added to an ethereal solution of phenylmagnesium bromide (bromobenzene, 1·0 g.; magnesium, 0·3 g.; ether, 100 c.c.), the orange-brown solution boiled for 2 hours under reflux, and the product decomposed with ice and ammonium chloride solution and then extracted with dilute hydrochloric acid. The yellowish-green aqueous layer on neutralisation yielded a precipitate of the *dihydroanthracene* derivative, which formed yellow needles (0·2 g.), m. p. 190°, from benzene (Found : N, 8·1. $C_{24}H_{26}ON_2$ requires N, 7·8%). It formed a yellowish-green solution in dilute hydrochloric acid; the colour was mainly due to the presence of traces of the colouring matter previously described.

Other meso-*Phenyl Derivatives of* 2 : 7-*Tetramethyldiaminoanthraquinone*.—Dyes similar to that described were obtained by replacing bromo(or chloro)benzene by α-bromonaphthalene, *p*-bromotoluene, and *p*-bromoanisole and also by methyl iodide. The methyl derivative, 2 : 7-tetramethyldiamino-10-hydroxy-10-methylanthrone, afforded deep bluish-green solutions in dilute mineral acids. The anthranol base formed colourless crystalline platelets from alcohol, m. p. 59—71°. The corresponding *p*-tolyl and *p*-anisyl derivatives were almost identical in colour with the phenyl derivative, but the α-naphthyl compound was appreciably darker. None of these substances was obtained sufficiently pure for analysis.

2 : 7-*Tetramethyldiamino*-9 : 10-*dihydroanthracene*.—To 3 : 3′-tetramethyldiaminodiphenylmethane (10 g.) in 15% hydrochloric acid (200 c.c.) was added 40% formalin (10 c.c.), and the mixture heated at 90° for 12 hours. On cooling and rendering the solution alkaline, a white crystalline precipitate was obtained (10·2 g.) which, recrystallised from alcohol, formed colourless needles, m. p. 198° (Found : C, 80·6; H, 8·0; N, 10·3. $C_{18}H_{22}N_2$ requires C, 81·2; H, 8·3; N, 10·5%), soluble in hot alcohol or glacial acetic acid, sparingly soluble in ether or carbon tetrachloride. With chloranil in boiling acetic acid a deep green substance was produced, but was not isolated in a pure form.

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