10. *Dinitrodibenzanthrone.*

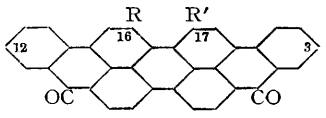
By D. J. Bennett, R. R. Pritchard, and J. L. Simonsen.

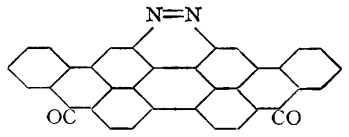
The authors have investigated the structure of dinitrodibenzanthrone and they find that, contrary to the views of Maki, Nagai, and Hayashi (*J. Soc. Chem. Ind. Japan*, 1935, **38**, 710B), the nitro-groups cannot be situated in the 16 : 17-positions. Since on oxidation with chromic acid a *dinitro*-2 : 2′-*dianthraquinonyl*-1 : 1′-*dicarboxylic acid* is obtained, it is suggested that it may be 3 : 12-dinitrodibenzanthrone.

By the nitration of dibenzanthrone in suspension in acetic acid either a mono- or a di-nitrodibenzanthrone or a mixture of these can be prepared depending upon the conditions employed. On reduction with alkaline hydrosulphite the corresponding mono- or di-amines are obtained and it is assumed (Cain and Thorpe, "Synthetic Dyestuffs," 7th Ed., p. 242) that the green dye (Caledon Green B) is an aminodibenzanthrone, yielding a black dye (Caledon Black) when oxidised on the fibre with sodium hypochlorite.

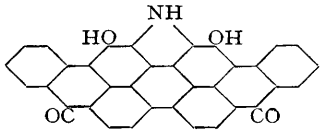
The nitration of dibenzanthrone has been studied in some detail by Maki, Nagai, and Hayashi (*loc. cit.*). They state that from nitrodibenzanthrone a dark blue dye, the monoamine, can be prepared, whereas the diamine, from dinitrodibenzanthrone, gives a green dye. They regard dinitrodibenzanthrone as the 16 : 17-derivative (I; R and R′ = NO_2), and the black dye obtained by oxidation of the diamine (I; R and R′ = NH_2) is considered to be the azine (II). In support of these structures they describe the oxidation of the diamine to a phenol formulated as containing the carbazole ring (III) and finally to a phenanthrapyrroledicarboxylic

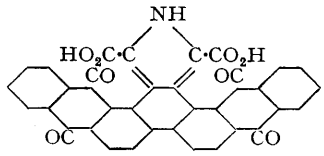
acid (IV). No direct evidence in support of these constitutions is advanced and the composition of (IV) was based apparently mainly upon a nitrogen estimation (N, 2·4%).

(I.) 



(II.)

(III.) 



(IV.)

It has therefore seemed to us desirable to obtain more conclusive evidence for the structure of the dinitrodibenzanthrone and we have examined the products formed by its oxidation with chromic acid. We find the main product to be an acid, from which the *methyl* and the *ethyl* ester were prepared. Although these esters, like the parent acid, are amorphous, their analyses leave no doubt that they are derived from an acid of the composition $C_{30}H_{12}O_{12}N_2$, a *dinitrodianthraquinonyl*-1 : 1′-*dicarboxylic acid*. This assumption was confirmed by the conversion of the nitro-acid into 2 : 2′-dianthraquinonyl-1 : 1′-dicarboxylic acid, the crystalline methyl ester of which decomposed at 374° and appeared to be identical in all respects with a specimen of the methyl ester of the acid obtained by the oxidation of dibenzanthrone.

These experiments show beyond doubt that the nitro-groups in dinitrodibenzanthrone cannot be in the 16 : 17-positions and we would suggest in analogy with other substitution reactions in the benzanthrone series (Cahn, Jones, and Simonsen, J., 1933, 445; Rule and Smith, J., 1937, 1098; Pritchard and Simonsen, J., 1938, 2047; Day, J., 1940, 1474) that they occupy the 3 : 12-positions but we can offer no proof of this. We have not attempted to determine the nature of the Japanese workers' phenol or dicarboxylic acid.

In view of the importance of obtaining for these experiments dibenzanthrone free from *iso*dibenzanthrone it was necessary to devise some method suitable for testing the homogeneity of our material. It was suggested to us by Dr. W. Rogie Angus that the determination of magnetic susceptibility might prove of value. We have used this method and we consider it to be of sufficient promise to warrant a further and thorough trial with similar intractable substances. We wish to express our thanks to Dr. Angus and to Mr. W. K. Hill, M.Sc., for making the measurements recorded below.

Experimental.

3 : 3′-*Dibenzanthronyl*.—This was purified by crystallisation from nitrobenzene and finally from *o*-dichlorobenzene until the magnetic susceptibility ($-0{\cdot}32 \times 10^{-6}$) was constant. The pure substance, decomp. 420°, after sintering at 412—415°, dissolved in sulphuric acid to give a carmine-red solution with an intense red fluorescence.

Dibenzanthrone.—Crude dibenzanthrone, after extraction with pyridine and with water (Soxhlet), was crystallised from cresol, in which it was very sparingly soluble, the apparatus described by Barrett, Dent, and Linstead (J., 1936, 1727) being used. The magnetic susceptibility ($-0{\cdot}540 \times 10^{-6}$) was constant after two crystallisations, remaining unaltered after three further crystallisations.

Dinitrodibenzanthrone.—To a suspension of finely powdered dibenzanthrone (10 g.) in acetic acid (150 c.c.) a solution of nitric acid (*d* 1·48; 60 c.c.) in acetic acid (90 c.c.) was added (mechanical stirring). The temperature of the mixture was raised during 1 hour to 60° and maintained thereat, with stirring, for 12 hours. The cooled mixture was poured into water (500 c.c.), and the solid (10 g.) collected, dried, and dissolved in sulphuric acid (*d* 1·84; 110 c.c.) at 60°, and water (30 c.c.) added with stirring, the temperature being kept below 70°. The dark blue microcrystalline solid (8 g.), which separated from the cooled solution, was collected, washed with sulphuric acid (80%) and then with water until free from mineral acid. After two crystallisations from nitrobenzene the violet solid had a magnetic susceptibility of $-0{\cdot}384 \times 10^{-6}$ (Found: N, 5·3. Calc. for $C_{34}H_{14}O_6N_2$: N, 5·1%). Dinitrodibenzanthrone dissolved in cresol or nitrobenzene to give a dark green solution; its colour in sulphuric acid was reddish-violet. It gave a blue vat having a strong red fluorescence, from which cotton was dyed green.

Dinitro-2 : 2′-*dianthraquinonyl*-1 : 1′-*dicarboxylic Acid*.—Dinitrodibenzanthrone (6 g.) was dissolved in sulphuric acid (*d* 1·84; 90 c.c.), and the cooled solution added gradually, with stirring, to a hot solution (95°) of chromic acid (22·5 g.) in water (675 c.c.). The mixture, well agitated by a current of air, was boiled for 12 hours, a further quantity of chromic acid (7·5 g.) being added after 4 hours. The cooled mixture was diluted with water (*ca.* 2 l.), and the solid, which separated, washed by decantation, collected and dissolved in aqueous ammonia. Acidification of the deep red ammoniacal solution precipitated the nitro-acid as a yellowish-brown solid (1·1 g.). This was best purified by precipitation from its solution in concentrated sulphuric acid (3 times) and solution of the product in warm aqueous ammonia, which removed a brown tar. Acidification of the ammoniacal solution gave the *nitro-acid* as a light brown, amorphous powder (0·5 g.) which did not melt below 400° and was very sparingly soluble in the usual organic media (Found: N, 5·1. $C_{30}H_{12}O_{12}N_2$ requires N, 4·7%). The *methyl* ester, prepared by the addition of an excess of ethereal diazomethane to a suspension of the acid in dioxan, was precipitated by the addition of methyl alcohol to its solution in methyl acetate as a pale yellow powder, blackening at 218° and gradually decomposing above this temperature (Found: C, 61·9; H, 2·7; N, 4·4. $C_{32}H_{16}O_{12}N_2$ requires C, 61·9; H, 2·6; N, 4·5%). The *ethyl* ester, prepared by the action of ethyl alcohol on the acid chloride, separated from alcohol–ethyl acetate as an amorphous orange-brown powder, which sintered at 169—173°, melted at 179—189° and decomposed above 190° (Found: C, 63·3; H, 3·2; N, 4·3. $C_{34}H_{20}O_{12}N_2$ requires C, 62·9; H, 3·1; N, 4·3%).

Methyl 2 : 2′-*Dianthraquinonyl*-1 : 1′-*dicarboxylate*.—(1) *From dibenzanthrone*. Dibenzanthrone (5 g.) was oxidised with chromic acid (22·5 g.) under conditions similar to those used for the oxidation of dinitrodibenzanthrone. The crude acid (1 g.) was a yellowish-brown amorphous powder. For purification, the acid (5 g.) was dissolved in sulphuric acid

(*d* 1·84; 25 c.c.), the solution kept at 100° for 10 minutes and poured into water (500 c.c.) and the pinkish-grey precipitate collected. This was dissolved in aqueous ammonia; the acid (4·3 g.) liberated from the filtered solution by acidification was a yellowish-brown powder. Three repetitions of this process gave a yellow powder (4·1 g.). This was extracted (Soxhlet) with dioxan, which left undissolved a dark tar, and deposited on cooling the nearly pure acid (2 g.) as a light brown powder. This was dissolved in dioxan (150 c.c.), and an excess of an ethereal solution of diazomethane added. After 24 hours in the ice-box, the somewhat sparingly soluble *methyl* ester had separated as a yellow powder (1 g.), decomp. 360—380°. The ester, after two crystallisations from nitrobenzene, was obtained in yellow leaflets, seen under the microscope to consist of characteristic square plates, decomp. 372° (Found: C, 72·7; H, 3·6. $C_{32}H_{18}O_8$ requires C, 72·5; H, 3·4%).

(2) *From dinitro-2 : 2'-dianthraquinonyl-1 : 1'-dicarboxylic acid.* The dinitro-acid (2 g.) in aqueous sodium hydroxide (2%; 150 c.c.) was added gradually with stirring to a suspension of ferrous hydroxide from ferrous sulphate, 15 g., in water, 150 c.c. After digestion for 1 hour, the ferric hydroxide was removed, the deep red filtrate acidified, and the amino-acid, a red amorphous powder, collected. To a solution of the amino-acid (2 g.) in sulphuric acid (*d* 1·84; 35 c.c.) at 20—25° a solution of sodium nitrite (5·3 g.) in sulphuric acid (100 c.c.) was added gradually (mechanical stirring) until a test portion on ice no longer deposited the amino-acid. Stirring was continued for another hour, and the diazonium salt precipitated as a brown powder by the addition of ice. The salt was collected, washed free from mineral acid with water and finally with alcohol, and then refluxed in amyl alcohol with zinc dust for 1·5 hours. The amyl alcohol was removed in steam, and the brown residue extracted with hot aqueous sodium hydroxide (2%). Acidification of the filtered alkaline solution gave the dianthraquinonyl acid as a brown powder. To remove unchanged amino-acid, the crude acid was dissolved in alkali and treated at 0° with potassium permanganate (1%) until an excess was present. This was removed by sulphur dioxide, and the acid (0·6 g.) recovered from the filtered solution. The methyl ester, prepared as described above, crystallised from nitrobenzene in yellow plates, decomp. *ca.* 374°, both alone and in admixture; the ester from two preparations was analysed (Found: C, 72·5, 72·1; H, 3·4, 3·6%).

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