XCV.—*Dyes Derived from Quinolinic Acid.*

By PRAPHULLA CHANDRA GHOSH.

THE object of the present investigation was to prepare dyes from quinolinic acid analogous to the phthaleins, and to compare their colour and fluorescence. That quinolinic acid condenses with phenol and resorcinol has, indeed, been mentioned by Noelting and Collin (*Ber.*, 1884, **17**, 258), but few details were given, and the products were not analysed. A compound from quinolinic acid and hydroxyquinol has been described by Liebermann and Wölbling (*Ber.*, 1902, **35**, 1786). In the present work, the condensation of quinolinic acid with resorcinol, catechol, phloroglucinol, *m*-phenylenediamine, *m*-dimethylaminophenol, and 2:4-diaminophenol has been effected. These condensations take place without the use of any condensing agent by simply heating the two constituents together.

In comparison with the corresponding phthaleins, the effect of the presence of the nitrogen atom in the ring is to lighten the colour and to diminish the fluorescence. In this series of compounds, the greater the power of an auxochromic group to deepen the colour, the greater is its effect on fluorescence. The compound obtained from quinolinic acid and *m*-dimethylaminophenol has the deepest colour and is the most strongly fluorescent.

Dyes analogous to hydroxyanthraquinones have not yet been prepared, but work in this direction is being continued.

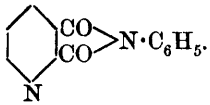
EXPERIMENTAL.

Quinolinic acid was prepared by oxidising a solution of quinoline (10 grams) in acetone (150 c.c.) with a 5 per cent. aqueous solution of the theoretical quantity of potassium permanganate at about 10°.

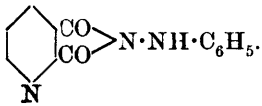
If the manganese dioxide is dried in the air, powdered, and then extracted with alcohol, the solution, on concentration, deposits pale yellow needles melting at 71—72°. This substance is insoluble in

alkali hydroxides and volatile with steam. The amount obtained was sufficient only for an estimation of nitrogen:

0·1145 gave 17·6 c.c. N_2 at 31° and 756 mm. N = 17·16 per cent.

Quinolinanil, 

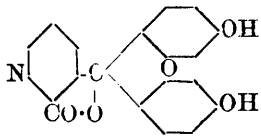
Half a gram of quinolinic acid and 2 c.c. of aniline were heated on the sand-bath for ten to fifteen minutes, when the whole of the acid dissolved. On cooling, crystals separated, which were collected and washed with alcohol. They formed colourless, prismatic needles melting at 248—251° (Engler, *Ber.*, 1894, **27**, 1789, gives 228°) (Found: N = 13·4. $C_{13}H_8O_2N_2$ requires N = 12·50 per cent.).

Quinolinylphenylhydrazine, 

Half a gram of the acid was heated with 2 c.c. of phenylhydrazine for about ten minutes. The clear solution, on cooling, became syrupy, and on adding alcohol, crystals were obtained which, when collected and washed free from phenylhydrazine, melted and decomposed at 237—238°:

0·099 gave 15·9 c.c. N_2 at 31° and 755 mm. N = 17·68.

$C_{13}H_9O_2N_3$ requires N = 17·55 per cent.

Resorcinolquinolinein, 

Two grams of quinolinic acid and 4 grams of resorcinol were heated at 180—200° for two hours. Some violet colouring matter sublimed, which might have been due to the formation of a substance resembling 1:3-dihydroxyanthraquinone. On cooling, the fusion was extracted with alcohol, and the dye was precipitated from the alcoholic extract with water. It could not be crystallised. It melts and decomposes at 266—267°. It is fluorescent in alcohol, acetone, or toluene, and aqueous potassium hydroxide gives an orange-green fluorescence:

0·1020 gave 0·2550 CO_2 and 0·032 H_2O. C = 68·1; H = 3·48.

$C_{19}H_{11}O_5N$ requires C = 68·46; H = 3·33 per cent.

The *silver* salt was prepared in the ordinary way:

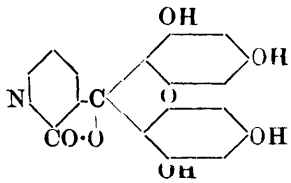
0·2132 gave 0·1092 AgCl. Ag = 38·6.

$C_{19}H_9O_5NAg_2$ requires Ag = 39·5 per cent.

Catecholquinolinein.

This compound has not yet been obtained in sufficient quantity for analysis. It is prepared and purified in the same way as the above compound. It dissolves in aqueous potassium hydroxide with a greenish-blue colour.

Phloroglucinolquinolinein,



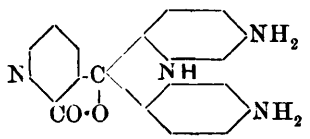
Two grams of quinolinic acid and 4 grams of phloroglucinol were heated at 130—150° for about ten minutes. At first the mixture melted, the colour changing to red, and then the whole solidified. On crystallisation from water, a red compound melting and decomposing at 275—277° was obtained, which was very readily soluble in alcohol:

0·100 gave 0·2277 CO_2 and 0·0289 H_2O. C = 62·1; H = 3·21.

$C_{19}H_{11}O_7N$ requires C = 62·46; H = 3·01 per cent.

If the solid mass is dissolved in alcohol and the solution concentrated, a pale yellow, crystalline compound is obtained which does not melt at 295°. It dissolves in aqueous potassium hydroxide with a yellow colour like the hydroxybenzophenones, and is more readily soluble in water than the compound just described. It has not been obtained in sufficient quantity for analysis.

m-*Phenylenediaminequinolinein,*



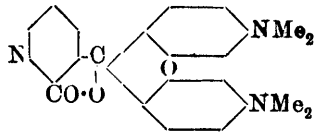
One gram of quinolinic acid and 3 grams of *m*-phenylenediamine hydrochloride were heated slowly to 210° and kept at 210—220° for twenty to twenty-five minutes. After cooling, the mass was extracted with alcohol and filtered; the solution was fluorescent.

The dye was obtained in a pure state by adding ether to the alcoholic solution. It melts and decomposes at 232—235°:

0·103 gave 15·4 c.c. N_2 at 30° and 758 mm. N = 16·73.

$C_{19}H_{14}O_2N_4$ requires N = 16·97 per cent.

m-*Dimethylaminophenolquinolinein*,

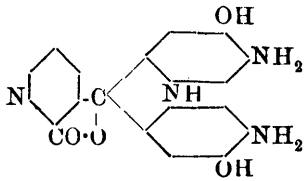


Quinolinic acid (0·75 gram) and *m*-dimethylaminophenol (1·5 grams) were heated at 120—130° for fifteen to twenty minutes, and then the temperature was slowly raised to 150°, when heating was stopped. The mass was extracted with alcohol, and the dye precipitated from the solution with water. When crystallised from dilute alcohol, it melted and decomposed at 148—151°. The alcoholic solution shows a reddish-violet fluorescence, which is deeper in acetic acid or alcoholic hydrochloric acid:

0·1062 gave 10·8 c.c. N_2 at 32° and 751·4 mm. N = 11·1.

$C_{21}H_{21}O_3N_3$ requires N = 11·5 per cent.

2:4-*Diaminophenolquinolinein*,



One gram of quinolinic acid and 3 grams of 2:4-diaminophenol hydrochloride were slowly heated to 180° and kept at this point for a few minutes. The dye was extracted by boiling with alcohol and filtering from the unchanged diaminophenol hydrochloride. It was purified by dissolving in alcohol and precipitating with water, but could not be crystallised. It does not melt at 290°. The compound is reddish-brown, and its solution in alcohol is fluorescent:

0·101 gave 13·8 c.c. N_2 at 30° and 756 mm. N = 15·37.

$C_{19}H_{14}O_4N_4$ requires N = 15·47 per cent.

In conclusion, I beg to express my great indebtedness to Sir P. C. Rây for the loan of 200 grams of quinoline.

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