Vat Dyes of Acenaphthene Series. IV. Condensation of Perylenetetracarboxylic Acid Anhydride with *o*-Phenylenediamine(1)

By Toshio MAKI and Harukichi HASHIMOTO

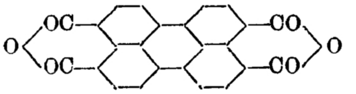
(Received July 5, 1952)

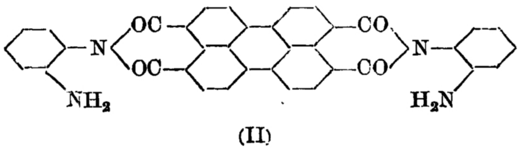
By the condensation of perylenetracarboxylic acid anhydride (I) with aromatic amines scarlet or red vat dyes of N, N'-diaryl-tetracarboxyldiimide type are generally obtained.(2) We have found, however, that the relation is quite particular in the case of *o*-phenylenediamine. At lower condensation temperature (160°) the main product (67.1% of the theory) was N, N'-di (*o*-amino) phenyl-perylenetetracarboxyl-diimide (II), which is soluble in alkaline hydrosulfite and insoluble in 90% sulfuric acid. It dyes cotton in weak, dull-red violet of low value as a vat dye.

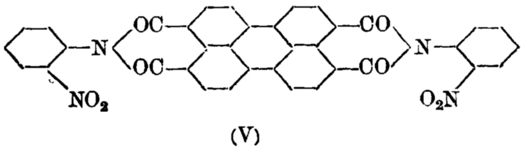
At moderate condensation temperature (190°) a new valuable violet vat dye was obtained as the principal product (60.6%), which is easily soluble in alkaline hydrosulfite and also soluble in 90% sulfuric acid. This dye has a very strong dyeing power and deep violet shade is produced on cotton with 2% dye (IW method). It is really remarkable that this new vat dye has the maximum light fastness (8 grade), highest of all-hitherto known synthetic organic dyes of violet shades. The fastness against chlorine is also maximum. The constitution of this dye is 3, 4-benzimidazole-9, 10-(*o*-amino) phenyl - perylenetetracarboxyl - diimide (III), simply called by us as "Acenaphthene Violet". The remaining amino group is diazotizable.

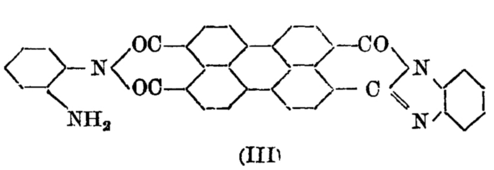
At the temperatures higher than 200° the main product is 3, 4, 9, 10-perylenetetracarboxyl-bis-benzimidazole (IV), which is a violet blue substance insoluble in alkaline hydrosulfite and for this reason it has no dyeing ability.(3)

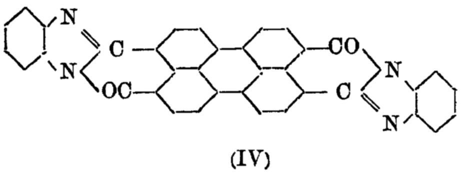
As another route N, N'-di (*o*-nitro) phenyl-perylenetetracaboxyl-diimide (V) was prepared by the condensation of perylenetetracarboxylic acid anhydride with *o*-nitroaniline and then


(I)


(II)


(V)


(III)


(IV)

---

(1) Read before the 5th Annual Meeting of the Chemical Society of Japan on April 5, 1952.

(2) T. Maki and H. Hashimoto, *J. Chem. Soc. Japan, Ind. Chem. Section*, **54**, 544 (1951).

(3) G. P. 502352, *Frdl.* **17**, 1395.

reduced with alkaline hydrosulfite containing sodium sulfide at 60°. The diamino compound thus obtained was completely identical with that (II), above mentioned, which had been prepared directly from *o*-phenylenediamine. The effect of thermal treatment on the stability of the three compounds is interesting. Thus, the diamino compound (II) is converted mainly into Acenaphthene Violet (III) by boiling with nitrobenzene for 1∼1.5 hours. Acenaphthene Violet can be almost entirely changed into the unvattable bis-imidazole (IV) when boiled with nitrobenzene for 5 hours. The quantitative separation of the three compounds can be carried out using alkaline hydrosulfite and 90% sulfuric acid.

Experimental Part

Condensation of Perlyenetetracarboxylic Acid Anhydride with *o*-Phenylenediamine.—A mixture of 1.96 g. (1/200 mole) of finely powdered perylenetetracarboxylic acid anhydride and 7.5 g. (14/200 mole) of *o*-phenylenediamine was kept in an oil bath without stirring for 4 hours at 190° (bath temperature). In order to remove the excess of *o*-phenylene diamine, 50 cc. of alcohol was added to the product, stirred at 70° for 30 minutes, filtered and washed with alcohol. From this residue the unchanged perylenetetracarboxylic acid anhydride was extracted by heating with 500 cc. of aqueous 1% sodium hydroxide on a water bath, filtering and thoroughly washing with water. Crude condensation product 2.77 g.

Separation.—The crude product was finely powdered, kept with 560 cc. (200 parts) of water, 11 g. (4 parts) of sodium hydroxide and 11 g. (4 parts) of sodium hydrosulfite at 45° for 15 minutes, filtered, and the residue was once more treated with the same amount of the alkaline hydrosulfite solution, filtered, washed with the alkaline hydrosulfite till the filtrate became colorless. The residue was then suspended in 500 cc. of water, acidified with hydrochloric acid, filtered and washed neutral. Yield (IV) is 0.41 g. (15.2% of the theory).

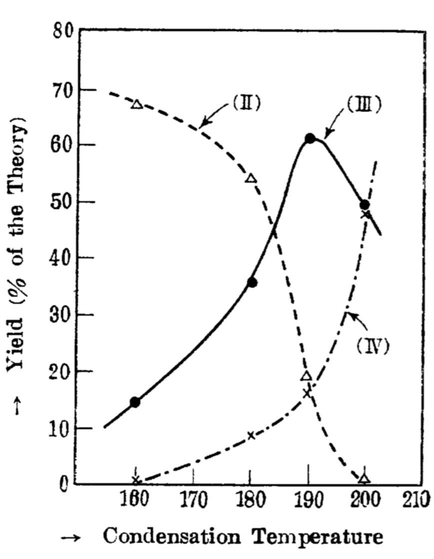


Fig. 1.

The combined violet red filtrate was oxidized by a current of air, the precipitate collected and washed neutral. Yield is 2.27 g. This was then dissolved in 115 g. (50 parts) of 98.7% sulfuric acid, 11.1 cc. of water added dropwise with external ice cooling to produce 90% sulfuric acid and allowed to stand over-night. The precipitate was collected on a glass filter, washed with 90% sulfuric acid, suspended in water and neutralized with sodium carbonate. Yield (II) is 0.55 g. (19.2% of the theory). The 90% snlfuric acid filtrate was poured into 1 l. of ice water, the resulting precipitate collected and washed neutral. Yield (III) is 1.68 g. (60.6% of the theory). The further relations between the condensation temperatures and yields of the three compounds are illustrated in Fig. 1.

3, 4 - Benzimidazolo- 9, 10 - (*o* - amino) phenylperylenetetracarboxyl - diimide (Acenaphthene Violet) (III).—Black violet powder, insoluble in organic solvents of lower boiling points, sparingly soluble in boiling *o*-dichlorobenzene or nitrobenzene with violet red color and weak red fluorescence. Soluble in conc. sulfuric acid and the solution shows blue (thin layer) and violet blue (thick layer) dichroism with weak red fluorescence. Soluble also in 90% sulfuric acid. Easily soluble in alkaline hydrosulfite and gives violet red vat with weak red fluorescence. Cotton is dyed in deep violet shade with 2% dye (IW method). These cotton dyeings have the maximum fastness against light (8 grade), chlorine (5 grade) and washing (40°—5 grade, 90°—4 grade). Staple fibre is dyed in deep red violet shade even with 1% dye. Found: N, 9.76; Calculated for $C_{36}H_{18}O_3N_4$ (III): N, 10.10%.

When the violet cotton dyeing was diazotized on the fibre and treated with alkaline β-naphthol solution the shade became more red and its light fastness suddenly depressed to 2 grade. By boiling 1.00 g. of the violet dye (III) with 2.0 g. of benzoyl chloride in 20 g. of *o*-dichlorobenzene under reflux for 10 hours 0.54 g. of insoluble violet powder and 0.50 g. of soluble violet red powder were obtained, apparently consisting of the bis-imidazole (IV) (the former) and benzoylated product of (III) (the latter). Both of them were no more vattable with alkaline hydrosulfite. When 1 part of Acenaphthene Violet (III) is heated with 200 parts of nitrobenzene at the boiling point (ca. 211°) for 5 hours the substance is nearly completely converted into the unvattable bis-imidazole (IV).

3, 4, 9, 10-Perylenetetracarboxyl- bis-benzimidazole (IV).—Violet grey powder, insoluble in organic solvents of lower boiling points, sparingly soluble in boiling nitrobenzene giving faint violet red solution with weak red fluorescence. Conc.

sulfuric acid solution is blue without dichroism and fluorescence, from which violet blue precipitate resulted by the addition of water. Insoluble in alkaline hydrosulfite. Found: N, 10.07; Calculated for $C_{36}H_{16}O_2N_4$ (IV): N, 10.44%.

N, N'-Di (*o*-amino) phenyl-perylenetetracarboxyl-diimide (II).—Red violet powder, insoluble in organic solvents of lower boiling points, sparingly soluble in boiling *o*-dichlorobenzene with violet red color and weak red fluorescence. Conc. sulfuric acid solution shows red violet (thin layer) and red (thick layer) dichroism with strong red fluorescence. The color of the sulfuric acid solution is changed into blue of the imidazoles when heated to 150°. Insoluble in 90% sulfuric acid. Soluble in alkaline hydrosulfite forming violet red vat with weak red fluorescence, from which cotton is dyed in weak dull red violet entirely different form the dyeings of (III). Found: N, 9.56; Calculated for $C_{36}H_{20}O_4N_4$ (II): N, 9.79%.

When the cotton dyeing was diazotized on the fibre and coupled with alkaline β-naphthol the shade was changed into red brown. By heating 1 part of the substance (II) with 200 parts of nitrobenzene at the boiling point for 1.5 hours 57% of the substance converted into Acenaphthene Violet (III) and 43% into the unvattable bis-imidazole (IV). If the boiling is continued for 5 hours the substance is nearly completely converted into the unvattable bis-imidazole.

Condensation of Perylenetetracarboxylic Acid Anhydride with *o*-Nitroaniline.—

N, N'-Di(*o*-nitro)phenyl-perylenetetracarboxyl-diimide (V).—Perylenetetracarboxylic acid anhydride (1.96 g., 1/200 mole) was heated with 6.90 g. (10/200 mole) of *o*-nitroaniline and 1.20 g. (4/200 mole) of glacial acetic acid in an oil bath under reflux with stirring at 230° (bath temperature) for 10 hours. The product was heated up with 50 cc. of alcohol and hot solution filtered. The collected precipitate was then treated with 200 cc. of hot aqueous 1% sodium hydroxide to remove the unchanged tetracarboxylic acid anhydride (recovered anhydride 0.48 g. or 24.4% of the starting material). Yield of (V) is 2.48 g. (78.5% of the theory). Dark brown powder, sparingly soluble in boiling nitrobenzene with red orange color and yellow fluorescence. Soluble in conc. sulfuric acid with strong red fluorescence and red violet (thin layer) and red (thick layer) dichroism. The color of the sulfuric acid solution is not changed into blue by heating to 150° and brown red precipitate is produced by pouring into water. Hydrosulfite vat (IW method) is violet red with weak red fluorescence and cotton is dyed in weak dull red violet, which is identical with the dyeing of the corresponding diamino compound. Found: N, 8.82; Calculated for $C_{36}H_{16}O_8N_4$ (V): N, 8.86%.

Reduction of N, N'-Di (*o*-nitro) phenyl-perylenetetracarboxyl-diimide.—The di (*o*-nitro) phenyl-diimide (V) (1.00 g.) was vatted by heating with 2.0 g. of sodium hydroxide, 2.0 g. of sodium hydrosulfite and 100 cc. of water to 60°, 0.80 g. of 55% sodium sulfide was added and kept further 2 hours at 60°. Water (100 cc.) was then added, oxidized by a current of air, the precipitate collected, thoroughly washed with water and dried at 110°. Yield is 0.84 g. Dark brown powder of violet red streak, soluble in conc. sulfuric acid with red violet (thin layer) and red (thick layer) dichroism and strong red fluorescence. All other chemical and dyeing properties are completely identical with the di (*o*-amino) phenyl-diimide (II) obtained directly with *o*-phenylenediamine. Converted also into Acenaphthene Violet (III) and then into the unvattable bis-imidazole (IV) by boiling with nitrobenzene.

Found: N, 9.45; Calculated for $C_{36}H_{20}O_4N_4$ (II); N, 9.79%.

Dyestuffs Research Laboratory, Department of Applied Chemistry, Tokyo University, Tokyo