102. *Some Green Pigments of the Phthalocyanine Series.*

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A number of tetraphenylphthalocyanines and tetrapyridylphthalocyanines and their copper derivatives have been prepared by standard methods from the corresponding phenyl- or pyridyl-phthalonitriles or phthalic acids. The preparation of various other intermediates for tetrapyridylphthalocyanine is also described. Both tetraphenyl- and tetrapyridyl-phthalocyanine are bright green pigments; the latter possesses basic properties and gives rise to water-soluble quaternary salts.

During investigations on the preparation of diaryl derivatives by means of the Gomberg and the related nitrosoacylarylamine reaction, whereby an aromatic amine $ArNH_2$ and a neutral aromatic compound Ar′H give rise to the product Ar·Ar′, use was made of 4-aminophthalonitrile as the aromatic amine. In the reaction between diazotised 4-aminophthalonitrile and benzene, carried out by the authors early in 1936, two unusual features were revealed. 4-Phenylphthalonitrile was formed in remarkably high yield (57% calculated on 4-aminophthalonitrile) for a reaction of this type, the product being almost entirely free from the tarry by-products which often occur in these reactions. Secondly, when an attempt was made to purify the crude 4-phenylphthalonitrile by high-vacuum distillation, the greater part of the almost colourless dinitrile was converted into an intensely green product, which was later shown to be a pigment of the phthalocyanine series.

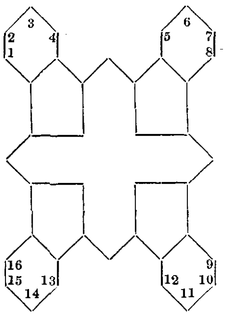
The blue pigment phthalocyanine is readily prepared from phthalonitrile (Linstead and Lowe, J., 1934, 1022) and on halogenation the shade becomes greener until, when sufficient halogen has been introduced, very bright pure green pigments are obtained (Barrett, Bradbrook, Dent, and Linstead, J., 1939, 1820). Certain substituted phthalocyanines such as the naphthalocyanines are also greenish in shade (Bradbrook and Linstead, J., 1936, 1744). After the discovery of the green tetraphenylphthalocyanine mentioned above, two patent specifications of the I.G. were published (B.PP. 470,499 and 470,542) which described the preparation of clear green phthalocyanine pigments of excellent fastness from *o*-dinitriles of the diphenyl, diphenylene oxide, and fluorenone series. Copper tetraphenylphthalocyanine was prepared as an amorphous dark green powder by heating 4-phenylphthalonitrile with cuprous chloride in presence of pyridine at 200—210°. The green pigments could be sulphonated and converted into colour lakes (B.P. 491,151). The 4-phenylphthalonitrile used in these examples was obtained from 3-nitro-4-aminodiphenyl *via* 3-nitro-4-cyano- and 3-amino-4-cyanodiphenyl, or from sodium 4-cyanodiphenyl-3-sulphonate by heating with anhydrous potassium ferrocyanide (B.P. 490,681).

4-*Phenylphthalonitrile* has now been prepared from diazotised 4-aminophthalonitrile and benzene by means of the Gomberg reaction and also by the action of 4-nitrosoacetamidophthalonitrile on benzene. A portion of the product was hydrolysed to the known 4-phenylphthalic acid. In similar manner a mixture of 4-o-, 4-m-, and 4-p-*methoxyphenylphthalonitriles* was formed when the benzene was replaced by anisole in the Gomberg reaction with 4-aminophthalonitrile. Nitration of 4-phenylphthalonitrile in a mixture of hot fuming nitric acid and glacial acetic acid gave, as the main product, 4-p-*nitrophenylphthalonitrile*, which on hydrolysis gave 4-*p*-nitrophenylphthalic acid. 4-Phenylphthalic acid has also been prepared from ethyl 4-nitrosoacetamidophthalate and benzene followed by hydrolysis.

Tetra-(4)-*phenylphthalocyanine* [*] and a mixture of isomeric *tetra*-(4)-*methoxyphenylphthalocyanines*, both products being intensely green pigments, were prepared respectively from 4-phenylphthalonitrile and a mixture of 4-*o*-, 4-*m*-, and 4-*p*-methoxyphenylphthalonitrile by heating with sodium ethoxide (cf. Linstead and Lowe, *loc. cit.*; Barrett, Dent, and Linstead, J., 1936, 1719), and *copper phthalocyanines* were prepared from the corresponding substituted phthalic acids (Butterworth, Heilbron, Hey, and Wilkinson, J., 1938, 1389) as well as from 3-phenylphthalic acid and a mixture of 4-*o*-, 4-*m*-, and 4-*p*-chlorophenylphthalic acid by heating with urea and cuprous chloride by Wyler's method (Wyler and I.C.I. Ltd., B.P. 464,126). Tetra-(4)-phenylphthalocyanine and its copper derivative gave a green shade similar to that of a copper chlorophthalocyanine, whereas the copper compounds of tetra-(3)-phenyl- and of tetra-(4)-chlorophenyl-phthalocyanine gave bluer shades.

The development of a new and convenient method for the preparation of arylpyridines (J., 1940, 349, 355, 358, 1279; Heilbron, Haworth, Hey, and I.C.I. Ltd., B.P. 518,886) led to the use of 4-aminophthalonitrile for the preparation of a mixture of 4-α-, 4-β-, and 4-γ-*pyridylphthalonitriles* from the reaction between the diazotised base and pyridine. Hydrolysis of a portion of the product with aqueous sodium hydroxide and subsequent heating of the resulting mixture of sodium salts with soda-lime gave a liquid product in which α- and γ-phenylpyridine were identified by treatment with picric acid and fractional crystallisation of the picrates. Specimens of pure 4-α- and 4-β-pyridylphthalonitrile were isolated from the mixture of nitriles by fractional precipitation with alkali from acid solution, and identified as such by hydrolysis, decarboxylation, and subsequent conversion into α- and β-phenylpyridine picrate. A number of other intermediates for the preparation of pyridylphthalocyanines have also been prepared. Mixtures of 4-α-, 4-β-, and 4-γ-*pyridylphthalimides* and 3-α-, 3-β-, and 3-γ-*pyridylphthalimides* were obtained from the interaction of the appropriate diazotised aminophthalimide with pyridine, as well as a mixture of *ethyl* 4-α-, 4-β-, and 4-γ-*pyridylphthalates* from diazotised ethyl 4-aminophthalate and pyridine (Heilbron, Haworth, Hey, and I.C.I. Ltd., B.P. 521,749), and mixtures of α-, β-, and γ-3 : 4-*dichlorophenylpyridine* and α-, β-, and γ-3 : 4-*dibromophenylpyridine* have been prepared from the appropriate diazotised 3 : 4-dihalogenoaniline and pyridine.

Metal-free *tetra*-(4)-*pyridylphthalocyanine* was prepared from a mixture of 4-α-, 4-β-, and 4-γ-pyridylphthalonitrile by heating it with sodium ethoxide, and the *copper* derivative was formed when the mixture of nitriles was heated with copper-bronze (cf. Bradbrook, Haworth, Heilbron, Hey, and I.C.I. Ltd., U.S.P. 2,277,629). It was subsequently shown (Haddock and I.C.I. Ltd., B.P. 530,881) that the same copper tetra-(4)-pyridylphthalocyanine could be prepared from tetra-diazotised copper tetra-(4)-aminophthalocyanine and pyridine. The resulting green pigment showed the anticipated basic properties and was soluble in glacial acetic acid and in strong mineral acids. When the tetrapyridylphthalocyanines are converted by normal methods into tetrapyridinium salts, new water-soluble dyes showing direct affinity for cotton and viscose artificial silk are obtained, which are bright blue-green to green in shade and fast to washing and light. This process of "quaternisation" provides a novel method for solubilising these pigments (Bradbrook, Coffey, Haddock, and I.C.I., Ltd., B.P. 522,293).



On account of resonance the phthalocyanine molecule is symmetrical in character and it is not possible to attribute a quinonoid structure to any one of the four benzene nuclei as is demanded by the static formula for the molecule. The assumption of a symmetrical basic structure simplifies the question of isomerism and the 16 aromatic hydrogen atoms in the parent compound (numbered 1 to 16 in the skeleton formula) may be divided into two groups of eight, *viz.*, those derived from a phthalic acid derivative substituted at position 3 and 4 respectively. Derivatives of 3-phenylphthalic acid thus give rise to four isomerides only, namely 1 : 5 : 9 : 13-, 1 : 5 : 9 : 16-, 1 : 5 : 12 : 16-, and 1 : 8 : 9 : 16-tetraphenylphthalocyanine, whereas derivatives of 4-phenylphthalic acid can give 2 : 6 : 10 : 14-, 2 : 6 : 10 : 15-, 2 : 6 : 11 : 15-, and 2 : 7 : 10 : 15-tetraphenylphthalocyanine. In the

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[*] The numbers given in parentheses refer to the orientation of the substituent in the parent phthalic acid derivative.

substituted tetraphenylphthalocyanines and the tetrapyridylphthalocyanines described in this communication the phthalocyanine structure may be attached to the substituted phenyl or pyridyl group at any one of three positions, and, further, the four groups may be all of the same kind or different. Such substituted tetraphenyl- and tetrapyridyl-phthalocyanines probably exist therefore in a relatively large number of different isomeric forms.

EXPERIMENTAL.

4-*Phenylphthalonitrile.*—*Method* (*a*). A suspension of 4-aminophthalonitrile (21 g.) in a mixture of hydrochloric acid (*d* 1·16; 60 c.c.) and water (30 c.c.) was diazotised in the normal manner with sodium nitrite (12 g.) in water (150 c.c.). Aqueous 20% sodium hydroxide was gradually added to a vigorously stirred mixture of the diazonium solution and benzene (300 c.c.) maintained at 5—10° until the mixture was slightly alkaline. Stirring was continued overnight, and the mixture allowed to attain room temperature. No tarry matter and very little coloured by-products were formed during the reaction. Evaporation of the separated benzene layer, after washing with dilute hydrochloric acid and with water, deposited the crude nitrile as an orange-coloured solid m. p. 145—155°. Crystallisation from dilute alcohol gave 4-*phenylphthalonitrile* in white needles (17 g.), m. p. 163—164° (Found : C, 82·2; H, 3·5. $C_{14}H_8N_2$ requires C, 82·35; H, 3·9%). An attempt was made to distil a portion of the crude nitrile in a vacuum, but a considerable proportion of it was converted into the green tetra-(4)-phenylphthalocyanine. A portion of the pure nitrile (1 g.) was boiled under reflux with a mixture of 70% sulphuric acid (15 c.c.) and glacial acetic acid (5 c.c.) for 3 hours. The mixture was poured into water, and the precipitated 4-phenylphthalic acid collected, dissolved in aqueous sodium hydroxide, filtered, reprecipitated with hydrochloric acid, again collected, and washed well with water. Crystallisation from dilute alcohol gave 4-phenylphthalic acid, m. p. 194°, both alone and on admixture with an authentic specimen (Found : C, 69·3; H, 4·0. Calc. for $C_{14}H_{10}O_4$: C, 69·4; H, 4·1%). Hydrolysis of the nitrile was also effected by refluxing with 10% aqueous sodium hydroxide for 2 hours.

Method (*b*). A 25% solution of nitrosyl chloride in acetic anhydride (26 g.) was added dropwise to a stirred suspension of 4-acetamidophthalonitrile (cf. Drew and Kelly, J., 1941, 640; 18 g.) in a mixture (250 c.c.) of glacial acetic acid and acetic anhydride (4 : 1) containing fused potassium acetate (10 g.) and a trace of phosphoric oxide at 8°. After a further 15 minutes the mixture was poured into excess of iced water, and the precipitated nitroso-compound collected and dried (yellow solid, m. p. 78°, decomp.). The nitroso-compound was added gradually to benzene (500 c.c.) at 60—70° and the mixture was maintained at this temperature for 2 hours. When cold the mixture was filtered from a small quantity of insoluble matter, and the filtrate evaporated. 4-Phenylphthalonitrile (7 g.) was deposited, m. p. 161—162° after crystallisation from alcohol, both alone and on admixture with the compound prepared by method (*a*).

4-o-, -m-, *and* -p-*Methoxyphenylphthalonitrile.*—A similar reaction to that described in method (*a*) was carried out with anisole (400 c.c.) in place of benzene. Separation of the anisole layer was facilitated by the addition of benzene, and the benzene–anisole layer was distilled on the steam-bath under reduced pressure, since if the anisole was removed by distillation at atmospheric pressure some phthalocyanine formation took place. Crystallisation of the crude residual nitrile from absolute alcohol gave a mixture of the three *nitriles* as a white crystalline solid, m. p. 112—134° (Found : C, 76·95; H, 4·45. $C_{15}H_{10}ON_2$ requires C, 76·9; H, 4·3%).

Nitration of 4-*Phenylphthalonitrile.*—A mixture of fuming nitric acid (10 c.c.) and glacial acetic acid (10 c.c.) was added gradually with stirring to a hot solution of 4-phenylphthalonitrile (2 g.) in glacial acetic acid (15 c.c.). Heating on the steam-bath was continued for 2 hours. After standing overnight a small quantity of insoluble matter (m. p. >300°) was removed, and the filtrate poured into water. Vacuum sublimation of the precipitated solid, followed by crystallisation from alcohol, gave 4-p-*nitrophenylphthalonitrile*, m. p. 228—229° (Found : C, 67·3; H, 3·2. $C_{14}H_7O_2N_3$ requires C, 67·4; H, 2·8%). F. P. 811,933 records m. p. 231° for this compound. Hydrolysis of a portion by boiling with 10% aqueous sodium hydroxide gave 4-*p*-nitrophenylphthalic acid, m. p. and mixed m. p. 178—179°.

4-*Phenylphthalic Acid.*—A solution of ethyl 4-acetamidophthalate (14 g.) was nitrosated with nitrosyl chloride as described in method (*b*) above. After being poured into excess of iced water, the nitroso-compound separated as a yellow oil, which was extracted with benzene. The extract was washed with water and kept over sodium sulphate for 12 hours at room temperature. Evaporation of the decanted solution left a brown oil, which was boiled for 3 hours with 20% aqueous sodium hydroxide (250 c.c.). After extraction with ether, acidification of the aqueous layer precipitated 4-phenylphthalic acid (5·5 g.), m. p. 194° after crystallisation from aqueous alcohol.

Tetraphenylphthalocyanines.—(a) *From the phthalic acids.* The phthalic acid (1 g.), urea (1 g.), cuprous chloride (0·15 g.), and a trace of ammonium vanadate were heated together at 200° for 1 hour. The fused mass was powdered and thoroughly extracted with hot water. The insoluble pigment was then further purified by continuous extraction with boiling *o*-dichlorobenzene. The above method was applied to 3- and 4-phenyl-, 4-(*o*, *m*, and *p*)-methoxyphenyl-, and 4-(*o*, *m*, and *p*)-chlorophenyl-phthalic acids (Butterworth, Heilbron, Hey, and Wilkinson, *loc. cit.*). The *copper* derivatives of tetra-(4)-phenyl- (Found : N, 12·4. $C_{56}H_{32}N_8Cu$ requires N, 12·7%), tetra-(3)-phenyl- (Found : N, 12·6%), tetra-(4)-methoxyphenyl- (Found : N, 10·9. $C_{60}H_{40}O_4N_8Cu$ requires N, 11·2%), and tetra-(4)-chlorophenyl-phthalocyanines (Found : N, 11·5. $C_{56}H_{28}N_8Cl_4$ requires N, 11·7%) were obtained as very dark green, amorphous powders.

(b) *From the phthalonitriles.* 4-Phenylphthalonitrile (2 g.) was heated for 10 minutes at 180° in presence of sodium ethoxide (0·1 g.). The molten mass became green. When cold, the fused mass was repeatedly extracted with hot water, and the insoluble green *tetra-*(4)-*phenylphthalocyanine* finally purified by extraction with boiling *o*-dichlorobenzene (Found : N, 13·9. $C_{56}H_{34}N_8$ requires N, 13·7%). A similar reaction with 4-methoxyphenylphthalonitrile gave *tetra-*(4)-*methoxyphenylphthalocyanine* (Found : N, 11·7. $C_{60}H_{42}O_4N_8$ requires N, 12·0%).

4-(*a*, *β*, *and γ*)-*Pyridylphthalonitrile.*—A suspension of 4-aminophthalonitrile (24 g.) in concentrated hydrochloric acid (70 c.c.) and water (30 c.c.) was diazotised at 0—5° with aqueous sodium nitrite (12 g.). The filtered diazonium solution was added dropwise during 2 hours to pyridine (200 c.c.) stirred at 25—30°. When addition was complete, stirring was continued for a further 2 hours, after which the brown solid (18 g.) which separated was filtered off, washed, and dried. An additional 3 g. was obtained on dilution and basification of the filtrate. After sublimation in a vacuum the white mixture of the three phthalonitriles was crystallised from alcohol (m. p. 155—165°) (Found : C, 76·2; H, 3·6. $C_{13}H_7N_3$ requires C, 76·1; H, 3·4%). Hydrolysis of a portion of the product with aqueous sodium hydroxide and evaporation to dryness gave a residue of sodium salts which was ground with soda-lime and heated strongly. The oily distillate was treated with alcoholic picric acid, and fractional crystallisation of the resulting picrates from acetone gave mainly α-phenylpyridine picrate, m. p. 174—175° and some γ-phenylpyridine picrate, m. p. 195—196°, both m. p.'s showing no depression on admixture with authentic specimens. The separation of pure 4-α- and 4-β-pyridylphthalonitrile from the mixture was effected by dissolving the crude product in hydrochloric acid, followed by fractional precipitation of the bases with aqueous sodium hydroxide. The first fraction, the 4-*a*-*pyridyl* compound, had m. p. 169° after crystallisation from alcohol (Found : C, 76·0; H, 3·5%) and, on hydrolysis and decarboxylation, as described above, gave α-phenylpyridine, identified as picrate, m. p. 175°. A subsequent fraction, the *β-analogue*, had m. p. 196—197° after crystallisation from alcohol (Found : C, 75·9; H, 3·5%), and, on hydrolysis and decarboxylation, gave β-phenylpyridine, identified as picrate, m. p. and mixed m. p. 160°.

4-(*α*, *β*, and *γ*)-*Pyridylphthalimides.*—A filtered solution of diazotised 4-aminophthalimide, prepared by gradual addition of sodium nitrite (12 g.) to a solution of the base (24 g.) in a mixture of concentrated sulphuric acid (25 c.c.) and water (40 c.c.) at 0—5°, was added during 2 hours to pyridine (200 c.c.) stirred at 40—50°. When addition was complete the reaction mixture was heated on the steam-bath for ½ hour and then poured into water (1000 c.c.). The yellow solid (18 g.) which separated was filtered off, washed with water, and dried. Purification by vacuum sublimation, followed by crystallisation from alcohol, gave a white mixture of the *pyridylphthalimides*, m. p. 238—246° (Found : C, 69·6; H, 3·9. $C_{13}H_8O_2N_2$ requires C, 69·6; H, 3·6%).

3-(*α*, *β*, *and γ*)-*Pyridylphthalimides.*—In similar manner 3-aminophthalimide (24 g.) gave these *imides* (27 g.) as a pale yellow solid. Vacuum sublimation followed by crystallisation from nitrobenzene gave the product as a white solid, m. p. 260—270° (Found : N, 12·0. $C_{13}H_8O_2N_2$ requires N, 12·5%).

Ethyl 4-(*α*, *β*, *and γ*)-*Pyridylphthalate.*—Ethyl 4-aminophthalate (38 g.) in a mixture of concentrated hydrochloric acid (80 c.c.) and water (8 c.c.) was diazotised at 5° with sodium nitrite (13 g.). The filtered diazonium solution was added slowly to pyridine (800 c.c.) stirred during 1½ hours at 50°. When addition was complete stirring was continued for 1 hour and the mixture left overnight. The dark solution was then neutralised with aqueous sodium hydroxide and excess of pyridine removed with steam. The non-volatile oil was extracted with benzene and separated. The viscous residue after removal of solvent was distilled in a vacuum and a mixture of the three *esters* (22 g.) was collected at 130°/0·01 mm. as a yellow oil (Found : C, 68·2; H, 5·9. $C_{17}H_{17}O_4N$ requires C, 68·2; H, 5·7%).

α-, *β*-, *and γ*-3 : 4-*Dichlorophenylpyridine.*—A diazonium solution, prepared by addition of aqueous sodium nitrite (14 g.) to a suspension of 3 : 4-dichloroaniline (32 g.) in concentrated hydrochloric acid (72 c.c.) and water (60 c.c.), was added during 2 hours to pyridine (250 c.c.) stirred at 30—40°. When addition was complete, the reaction mixture was heated on the steam-bath for ½ hour and then made alkaline with ammonia. Excess of pyridine was removed with steam. The non-volatile viscous oil was extracted with benzene. After removal of the solvent the mixed α-, β-, and γ-3 : 4-*dichlorophenylpyridines* (19 g.) were collected at 170—200°/1 mm. as a pale yellow solid, m. p. 60—70°, after crystallisation from light petroleum (b. p. 40—60°) (Found : C, 59·4; H, 3·1. $C_{11}H_7NCl_2$ requires C, 59·6; H, 3·1%).

α-, *β*-, and *γ*-3 : 4-*Dibromophenylpyridine.*—The diazonium solution, prepared by addition of aqueous sodium nitrite (7 g.) to a suspension of 3 : 4-dibromoaniline (25 g.) in concentrated hydrochloric acid (36 c.c.) and water (36 c.c.) at 0—5°, was added gradually to pyridine (150 c.c.) stirred at 30—40°. The product was worked up as described in the preceding paragraph, and the mixture of the three *bromo-compounds* was collected at 140—170°/<1 mm. and solidified on cooling. Crystallisation from light petroleum (b. p. 40—60°) gave a microcrystalline product, m. p. 60—70° (Found : C, 42·5; H, 2·6. $C_{11}H_7NBr_2$ requires C, 42·2; H, 2·2%).

Tetrapyridylphthalocyanines.—Metal-free tetra-(4)-pyridylphthalocyanine was prepared by heating 4-(α, β, and γ)-pyridylphthalonitrile (2 g.) with sodium ethoxide (0·1 g.) at 180° for 15 minutes. The cold fused mass was repeatedly extracted with hot water, and the insoluble pigment finally extracted with boiling *o*-dichlorobenzene. *Tetra*-(4)-*pyridylphthalocyanine* was obtained as a greenish-black, amorphous powder (Found : N, 19·9. $C_{52}H_{34}N_{12}$ requires N, 20·3%). The copper derivative was formed by heating a mixture of 4-(α, β, and γ)-pyridylphthalonitrile (1·6 g.) and copper bronze (0·14 g.) in a Pyrex tube in an oil-bath at 220° with stirring. The mixture became semi-solid and after 15 minutes it was allowed to cool. The resulting *copper tetra*-(4)-*pyridylphthalocyanine* was extracted with pyridine, in which it gave a deep green solution and from which it separated as a dark blue-green, amorphous powder on concentration (Found : N, 19·0. $C_{52}H_{32}N_{12}Cu$ requires N, 19·3%). The pigment was also soluble in glacial acetic acid and in strong mineral acids.

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