197. *Phthalocyanines and Related Compounds. Part XIX. Tetrabenzporphin, Tetrabenzmonazaporphin and their Metallic Derivatives.*

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The paper is concerned with the preparation of macrocyclic pigments analogous to phthalocyanine, but containing three or four methin links, from intermediates containing one real or potential *iso*indole residue.

Tetrabenzmonazaporphin has been prepared for the first time from intermediates derived from phthalonitrile both by the Thorpe reaction and by the Grignard reaction. Its structure has been proved by quantitative oxidation and a number of its metallic derivatives have been prepared.

Zinc tetrabenzporphin can readily be prepared from 3-carboxymethylphthalimidine. From it tetrabenzporphin has been obtained and thence a number of metallic derivatives. The structure has been proved by quantitative oxidation. A number of other reactions giving rise to these macrocyclic compounds are described.

The absorption spectra of all these compounds have been measured quantitatively, and the results are compared with those for the analogous phthalocyanine and tetrabenztriazaporphin derivatives.

The compounds are compared with those recently obtained by Helberger and his co-workers. The various methods available for their preparation are reviewed, and possible mechanisms are discussed.

This paper describes the continuation of our investigations of the group of macrocyclic pigments of the general formula $[C_{32}H_{18}N_4 + x(N) + (4 - x)(CH)]$.

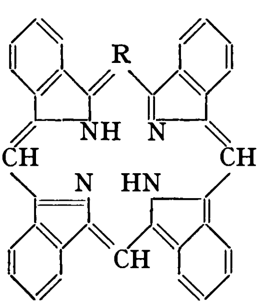
Our first attempts (Linstead and Noble, J., 1937, 933) at the preparation of tetrabenzporphin, the symmetrical analogue of phthalocyanine containing four methin links ($x = 0$), were unsuccessful, probably owing to the lack of thermal stability of the intermediates examined. Since then we have been successful in obtaining the corresponding compound containing one methin link ($x = 3$) (Barrett, Linstead, and Tuey, J., 1939, 1809).

The present paper describes the solution of the problem attacked in 1937. Tetrabenzporphin (I, R = CH) and tetrabenzmonazaporphin (I, R = N) and various of their metallic derivatives have been prepared by comparatively simple methods. In the meantime Helberger and his collaborators, by different reactions, have made tetrabenzporphin and certain metallic derivatives of tetrabenzmonazaporphin. Later in this paper the mechanism of the formation of these large molecules from intermediates containing one *iso*indole unit is discussed. To clarify this discussion a brief summary of the most important preparative methods used by other workers becomes necessary.

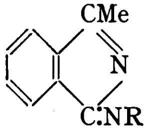
Helberger (*Annalen*, 1937, **529**, 205) obtained the copper derivatives of tetrabenzmonaza- and -diaza-porphin, in 10 and 20% yields respectively, by heating an *o*-halogenoacetophenone with cuprous cyanide, respectively with and without phthalonitrile. Later, pre-formed *o*-cyanoacetophenone was used with similar results (Helberger and von Rebay, *Annalen*, 1937, **531**, 279). A better yield of pigment was obtained by Dent (J., 1938, 1), who used 3-methylenephthalimidine, the cyclic isomeride of cyanoacetophenone. From a mixture of this or its carboxylic derivative, phthalonitrile and copper, Dent obtained copper tetrabenztriazaporphin in 30% yield. He was unable to obtain a pigment with more than one methin link from these intermediates, but Helberger and Hevér (*Annalen*, 1938, **536**, 173) have recently shown that the acid * gives traces of tetrabenzporphin derivatives when heated with magnesium, magnesium acetate, or zinc acetate. Not unexpectedly, the pigments obtained from cyanoacetophenone tend to be mixtures. From the product of its reaction with iron, Helberger, von Rebay, and Hevér (*Annalen*, 1938, **533**, 197) were able to separate ferrous tetrabenzporphin in small amount. Subsequently they found that methylphthalimidine gave small yields of homogeneous tetrabenzporphin derivatives when heated with metals or metallic acetates.

Obviously, none of these reactions approaches in ease or completeness those which lead to the production of phthalocyanines. The yields tend to fall with the number of methin links involved. An immediate object of our work was therefore to make these interesting compounds readily available by finding preparative methods which would give reasonable yields from accessible intermediates.

I. *Tetrabenzmonazaporphin* ($x = 1$).—The effective intermediate in the production of tetrabenztriazaporphin from phthalonitrile by means of the Grignard reaction (Barrett, Linstead, and Tuey, *loc. cit.*) is probably a metallic derivative such as (II ; R = MgI or Li).



(I.)



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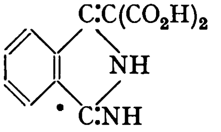

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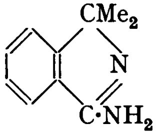

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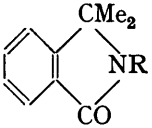

(V.)

It is possible to obtain from phthalonitrile, by means of the Thorpe reaction, a compound of very similar structure in 1-imino-3-dicarboxymethylenephthalimidine (III, see Barrett and Linstead, preceding paper). It is found that both this substance and its diethyl ester

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* The acid intermediate used by Dent was actually *o*-carbamylbenzoylacetic acid (Linstead and Rowe, this vol., p. 1071).

yield pigments, whereas none can be obtained from the corresponding keto-ester, formed by the hydrolysis of the imino-group.

The imino-malonic ester (corresponding to III) when fused with copper, or with a mixture of phthalonitrile and cupric chloride, gives poor yields of copper pigments. The imino-malonic acid (III) is of much greater use. It gives pigment readily when fused with a variety of metals and metallic acetates, but little or none with chlorides or oxides. These products are essentially derivatives of tetrabenzmonazaporphin, although under certain conditions it is possible to obtain a tetrabenzporphin derivative from the imino-acid.

Fusion of the imino-acid with zinc yielded a green compound containing zinc. The metal could be removed by passing hydrogen chloride through a solution of the substance in sulphuric acid. The product was *tetrabenzmonazaporphin*, $C_{35}H_{21}N_5$ (I, R = N), the over-all stoicheiometric yield 27%. The compound crystallised in green needles with a violet-blue lustre. Like phthalocyanine and tetrabenztriazaporphin, it could be sublimed at high temperatures. It was converted into its ferrous, copper, *magnesium*, and zinc derivatives by treatment with ferrous chloride and the appropriate metals respectively. The copper and ferrous derivatives had already been made by Helberger and his co-workers (*loc. cit.*). The absorption spectra of these substances are reviewed later in detail: our values for the last two compounds tallied fairly closely with those of Helberger.

Lithium phthalocyanine is freely soluble in alcohol (Barrett, Frye, and Linstead, J., 1938, 1157). Metal-free tetrabenzmonazaporphin, when boiled with alcoholic lithium ethoxide, yielded a deep green solution, but most of the solid remained undissolved, even when a large excess of the reagent was used. It appears, therefore, that the lithium derivative is easily reconverted into the parent compound by alcohol.

The formulation of the new pigment as of the phthalocyanine type is clearly indicated by the analysis, general properties, high stability and intense and sharply banded absorption spectrum. We have confirmed the structure by the method of quantitative oxidation successful for phthalocyanine (Dent, Linstead, and Lowe, J., 1934, 1033) and for tetrabenztriazaporphin. By analogy with previous results, complete oxidation should follow the equation:

$$C_{35}H_{21}N_5 + H_2O + 13O = 4C_8H_5O_2N + 3CO_2 + NH_3$$

Experiment showed that the oxidation was more difficult than that of the more nitrogenous pigments. Under suitable conditions it was, however, possible to obtain complete oxidation and reasonably reproducible figures for the oxygen uptake by the use of ceric sulphate. Tetrabenzmonazaporphin required 12·5 g.-atoms of oxygen per mol., and its copper derivative 12·6 g.-atoms, in close agreement with theory.

It was pointed out in our paper on the triaza-analogue that it was impossible from analytical data alone to decide whether macrocyclic substances such as these were actually homogeneous compounds with " mixed links "—some methin, some nitrogen—or mixtures of very similar compounds. For example, the monaza-compound might contain tetrabenzporphin, compensated analytically by some more nitrogenous substance. This possibility is excluded by the spectroscopic evidence. The absorption spectrum of tetrabenzporphin shows a sharp triplet in the orange region with $\lambda_{max.}$ 6210, 6120, and 6040 A. The spectrum of tetrabenzmonazaporphin has a duplet in about this region ($\lambda_{max.}$ 6260, 6100 A.), rather weaker in intensity, and there is no sign of a third band. Evidence from the spectra of the metallic derivatives supports this. The method of preparation is not one which might, *a priori*, be expected to give a homogeneous pigment. However, in the absence of any definite evidence to the contrary (except the slightly low oxidation value), we can take the analytical data at their face value and accept the pigment obtained from the imino-malonic acid (III) and zinc as authentic tetrabenzmonazaporphin.

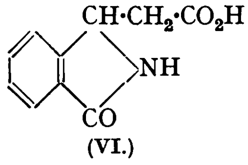
If zinc acetate is fused with the same acid, the resulting pigment is undoubtedly a mixture. After removal of the metal and crystallisation, the product gave analytical figures corresponding with a mixture of tetrabenzmonazaporphin (60%) and tetrabenzporphin (40%). Moreover, the oxidation value was high (*ca.* 13·5 g.-atoms) and the absorption spectra showed both monaza- and tetrabenz-porphin bands. Confirmatory results were obtained by examining the zinc compound formed in the fusion. The action of copper, magnesium, or magnesium acetate on the imino-acid (III) gave pigments in yields of about 40% which have not yet been fully investigated, but appear to be mixtures of tetrabenz-monaza- and -diaza-porphin derivatives. When mixtures of phthalonitrile and the imino-acid (III) were fused with metallic reagents, more nitrogenous pigments were formed. One mol. of phthalonitrile reacted with 3 mols. of the acid and copper bronze to give nearly pure copper tetrabenztriazaporphin. A similar mixture, with zinc in the place of copper, gave a pigment approximating to the diazaporphin in composition. It appears that zinc, either as such or as zinc acetate, is the metal most favourable to the formation of methin links.

Tetrabenzmonazaporphin can also be conveniently prepared by means of the Grignard reaction. It was shown by Barrett, Linstead, and Tuey (*loc. cit.*) that the product of the reaction between equivalent proportions of methylmagnesium iodide and phthalonitrile, when heated to a high temperature with a little water, gave a 40% yield of tetrabenztriazaporphin. It is now found that, if a considerable excess of methylmagnesium iodide ($2\frac{1}{2}$ mols.) is employed and the primary product treated with steam at 200°, a yield of some 17% of tetrabenzmonazaporphin is obtained. It is known (*loc. cit.*) that 1 : 1-dimethyl-3-amino-*ψ-iso*indole (IV) can be isolated from the product of the action of an excess of methylmagnesium iodide on phthalonitrile. This base yields a mixture of the zinc derivatives of the monaza-compound and of tetrabenzporphin when it is heated vigorously with zinc acetate, but we think it doubtful if it is the actual intermediate in the formation of monaza-pigment from the Grignard product.

During the reaction between zinc acetate and 1 : 1-dimethyl-3-amino-*ψ-iso*indole, a colourless distillate was formed, which deposited a crystalline solid, m. p. 162°, of composition $C_{10}H_{11}ON$. The same compound was formed when dimethylamino-*ψ-iso*indole was acetylated with acetic anhydride, and the product hydrolysed with hydrochloric acid. The intermediate acetyl derivative was not formed normally, an imino-group being replaced by an oxygen atom during the reaction. It seems probable that the intermediate is 2-*acetyl*-3 : 3-*dimethylphthalimidine* (V, R = $CO{\cdot}CH_3$), and that the compound of m. p. 162° is 3 : 3-*dimethylphthalimidine* (V, R = H). The behaviour of the base on acetylation differs from that of dibenzylamino*iso*indole, which, according to Weiss and Freund (*Monatsh.*, 1924, **45**, 105), yields a normal diacetyl derivative. In an attempt to confirm the structure of dimethylphthalimidine by synthesis, dimethylphthalide was treated with ammonia under a variety of conditions. No reaction occurred. The resistance of this substituted molecule to the action of ammonia is in interesting contrast to the ready reaction of phthalide itself and of its unsaturated derivatives.

Dimethylphthalimidine gave only a trace of benzporphin pigment when heated with zinc acetate.

II. *Tetrabenzporphin* ($x = 0$).—An examination of the compounds described by Linstead and Rowe (*loc. cit.*) showed that two were useful intermediates for the formation of macrocyclic pigments. These were 3-carboxymethylphthalimidine (VI) and the equivalent β-hydroxy-β-*o*-carbamylphenylpropionic acid, which yields the cyclic acid (VI) at 105°. When the acid (VI) was heated above 300° with zinc or zinc acetate, it readily yielded zinc tetrabenzporphin. The zinc pigment could be obtained analytically pure by crystallisation or sublimation. Similar green compounds were formed in worse yield from the acid (VI) and magnesium or iron, but none at all by means of copper. The magnesium derivative was isolated in a solvated form in agreement with Helberger, von Rebay, and Hevér (*loc. cit.*). During the fusions a purple condensate appeared in the cooler parts of the reaction vessel. Helberger and his co-workers observed a red sublimate in their preparations from methylphthalimidine.



(VI.)

The process constitutes the most convenient synthesis of a compound containing the porphyrin ring, for it involves only three stages from a commercially accessible intermediate (nitroso-β-naphthol). The stoicheiometric yield, although low, appears to be an improvement over that obtained from methylphthalimidine.

Tetrabenzporphin (I, R = CH) was isolated from the zinc derivative by passing hydrogen chloride through its sulphuric acid solution, and could be purified by crystallisation and sublimation. Helberger reports that the metal is removed by the action of sulphuric acid alone. In our hands this certainly gave a considerable elimination of metal, but the auxiliary use of hydrogen chloride was necessary to obtain a completely ash-free product. The metal-free compound was converted into its copper and iron derivatives by means of cuprous and ferrous chlorides in quinoline. Apart from minor differences, these compounds were identical in absorption spectra with the corresponding compounds made by Helberger's method.

o-Cyanocinnamic acid, which is related to 3-carboxymethylphthalimidine (*iso*indolinone-3-acetic acid) (F. M. Rowe, Haigh, and Peters, J., 1936, 1101; Linstead and G. A. Rowe, *loc. cit.*), yields rather impure zinc tetrabenzporphin in poor yield when fused with zinc acetate. The corresponding saturated acid, β-*o*-cyanophenylpropionic acid (Part XVII) gives no macrocyclic pigment.

The structure of tetrabenzporphin was confirmed by quantitative oxidation with acid ceric sulphate. The equation:

$$C_{36}H_{22}N_4 + 17O = 4C_8H_5O_2N + 4CO_2 + H_2O$$

requires an uptake of 17 g.-atoms of oxygen, leading to a liberation of 4 mols. of carbon dioxide. Experiment showed a strong resistance to oxidation,* an even longer period being required than for tetrabenzmonazaporphin, and the reproducibility of the results was not so good. The uptake of oxygen by the metal-free compound was 16·2 g.-atoms, and by the zinc derivative, 17·1 g.-atoms. The carbon dioxide was estimated by a slight modification of the method used for the estimation of the methin link of tetrabenztriazaporphin. Zinc tetrabenzporphin yielded 3·97 mols. of carbon dioxide on oxidation. Attempts at the quantitative estimation of the phthalimide formed were fruitless, as it was partially hydrolysed under the rigorous conditions necessary to complete the oxidation. We believe that this is the first example of the quantitative oxidation of an actual porphyrin ring.

Tetrabenzporphin being a symmetrical compound, the results of oxidation and the analytical figures provide unambiguous evidence as to the structure.

For comparison with the materials prepared by our methods, we have prepared samples of the copper derivatives of tetrabenz-monaza-, -diaza- and -triaza-porphin from *o*-cyanoacetophenone (the preparation of which has been improved) and also of zinc tetrabenzporphin from methylphthalimidine by Helberger's methods (*loc. cit.*). The tetrabenzporphin derivative was homogeneous and identical with ours. The copper monaza-pigment from cyanoacetophenone was also substantially homogeneous. On the other hand, the copper pigments prepared from mixtures of phthalonitrile and cyanoacetophenone were not homogeneous. The diaza-compound contained a considerable proportion of triaza-, and the triaza-derivative was contaminated with a small amount of diaza-. We used a slightly different method for the purification of the products; but it is clear (and not unexpected) that these mixed fusions are not satisfactory for the preparation of homogeneous material.

III. *Absorption Spectra.*—Quantitative measurements have been made of the absorption spectra of tetrabenzporphin and tetrabenzmonazaporphin and their metallic derivatives. To complete the comparison with other pigments of the group, we have measured the intensities of the absorption bands of a number of metallic phthalocyanines and metallic tetrabenztriazaporphins. The detailed results are given in the experimental section.

The nature of the solvent used for many of these measurements was important. Chloronaphthalene has the advantage that it dissolves all the pigments of the group sufficiently for the measurements, even the sparingly soluble phthalocyanines. It was, however, unsatisfactory for the zinc, and more particularly for the magnesium, derivatives of tetrabenz-porphin and -monazaporphin because the intensities of the absorption bands of such solutions changed on standing, and at the same time the green colour of the solutions slowly changed to brown. Solutions of the same compounds in pyridine–ether showed no such decrease in intensities. It seems probable that this effect is due to a liberation of hydrogen chloride from the solvent, and its fixation by the zinc pigment as a salt. It may be recalled that zinc chlorophthalocyanine forms a fairly stable hydrochloride (Barrett, Dent, and Linstead, J., 1936, 1720). In support of this, it was found that, if benzene saturated with

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* Helberger and co-workers observed a strong resistance of tetrabenzporphin towards nitric acid.

hydrogen chloride was added to a fresh solution of zinc tetrabenzporphin in chloronaphthalene, the green colour of the solution was at once changed to brown. Solutions of zinc phthalocyanine and zinc tetrabenztriazaporphin in chloronaphthalene are considerably more stable. This instability, therefore, is met with principally among derivatives of the more basic macrocyclic pigments, *i.e.*, those containing fewest nitrogen links. Solutions of ferrous and of magnesium phthalocyanine in chloronaphthalene also show a fading of the spectral bands on standing, but this is also shown in pyridine–ether solutions and is probably due to aerial oxidation (compare Cook, J., 1938, 1174, 1845). We have not so far observed fading in intensities (during the same periods of standing) with solutions of any metal-free or copper macrocyclic pigment, either in chloronaphthalene or in a basic solvent.

It has been observed among porphyrins by Stern and his co-workers that in general the nature of the solvent does not affect the position of the bands, and this is also true of phthalocyanine (Anderson, Bradbrook, Cook, and Linstead, J., 1938, 1151). The same independence of solvent is shown by the metal-free and copper compounds described in the present paper. On the other hand, the spectra of solutions of the iron, zinc, and magnesium derivatives in basic solvents differ from those in chloronaphthalene in respect to both the positions of the band heads and particularly their intensities. This is undoubtedly due to solvation. Many examples of the crystallisation of iron and magnesium compounds of macrocyclic pigments in a solvated form from bases are on record (*e.g.*, Linstead and Lowe, J., 1934, 1022; Barrett, Frye, and Linstead, *loc. cit.*; Helberger, von Rebay, and Hevér, *loc. cit.*).

The absorption spectra of the magnesium and zinc derivatives of tetrabenz-porphin and -monazaporphin in pyridine–ether are all very complex, having at least nine bands in the visible region. The spectra of the magnesium and zinc derivatives of tetrabenzporphin in this mixture of solvents (see p. 1091) have two particularly remarkable features. First, they are indistinguishable in the positions of all nine of the band heads and in order of the intensities. The extinction coefficients of the magnesium pigment are, however, slightly lower than those of the zinc derivative. Secondly, the 4360 bands are of a quite exceptional intensity, with extinction coefficients of about 600,000.

The table summarises the properties of the four known metal-free macrocyclic pigments of the phthalocyanine type $C_{32}H_{18}N_4 + xN + (4 - x)CH$:

Compound	Phthalocyanine	Tetrabenztri-azaporphin	Tetrabenzmon-azaporphin	Tetrabenz-porphin
x	4	3	1	0
Oxidation.				
G.-atoms of O used { calc. $1 + 4(4 - x)$	1	5	13	17
found	1·0	4·8	12·5	16·2
G.-mols. of CO_2 formed { calc. $(4 - x)$	0	1	3	4
found	0·1	0·9	—	4·0 *
Time necessary for completion	Rapid at 60°	20 mins. at 100°	30 mins. at 100°	40 mins. at 100°
Colour in H_2SO_4	Brown	Brown	Green	Green
1 Drop of HNO_3 added to H_2SO_4 solution	Transitory red, rapidly decolourised	Red, fading slowly	Dull Prussian-blue, changing to red-brown	Blue-black, changing to red-brown
Solubility in organic media	Increases →			
Ease of sublimation	← Increases			
λ of main bands in red	← Increases			
Intensity of bands in violet	Increases greatly →			
Acidity (firmness with which metals are held)	← Increases			
Basicity (tendency to salt-formation with acids)	Increases →			
Preparation and yield †	Over 90% from phthalonitrile	40% from Grignard reaction ‡	27% from 1-imino-3-dicarboxymethylene-phthalimidine § (III)	*ca.* 20% from 3-carboxymethylphthalimidine §

* Zinc derivative. † Of the metal-free compound or a metallic derivative. ‡ Barrett, Linstead, and Tuey, *loc. cit.* § This paper.

There is a satisfactory general agreement between our spectroscopic results and those of Helberger and his collaborators, as far as comparison is possible. They did not, however, observe many of the intense bands in the violet region, and a number of the weaker bands elsewhere.

A few additional empirical observations may be added to those already made in earlier papers on the effect of the nature of the linking groups and of the central metals on the spectra of macrocyclic pigments. As the number of methin links increases, the bands in the blue-violet region (which are very faint in the triaza-compounds) become stronger without appreciable shift in position, until in tetrabenzporphin and its derivatives they are dominant. At the same time, the bands in the red region show a shift towards lower wave-length. A characteristic feature of the spectrum of metal-free tetrabenzporphin, when viewed visually, is the sharp triplet at 6210, 6120, and 6040 A., the three bands having almost equal intensities. The entry of metal (in the absence of the solvation effects already noted) tends to simplify the spectrum. Thus in copper tetrabenzporphin the triplet has as counterpart a single band at 6280 A. with inflexions on the short wave side. Again, the intense and sharp duplet in the violet region of the spectrum of tetrabenzporphin (λ 4380 and 4220 A.) is modified by the introduction of copper to a rather broader single band (λ 4260 A.). This simplication is particularly noticeable with the iron derivatives of tetrabenz- and tetrabenzmonaza-porphin, which have only three or four bands in the spectrum which can be detected visually.

IV. *Mechanism of Pigment Formation.*—The formation of macrocyclic pigments with methin links invariably involves a high temperature, and results in a relatively small yield, even under the most favourable conditions; the mechanism of such reactions must necessarily be somewhat uncertain. Nevertheless, two stages must be involved: (1) The linking together of single *iso*indole units to form a chain, and (2) the cyclisation to give the great ring. The latter stage is the more obscure; it might reasonably occur (see Part XV) by an initial cyclisation to a dehydro-compound, followed by fixation of metal. The mechanism of the first stage is more susceptible to experimental attack.

In Part XV (Barrett, Linstead, and Tuey, *loc. cit.*), we postulated a chain mechanism to explain the formation of tetrabenztriazaporphin from a product of the Grignard reaction on phthalonitrile such as (II; R = MgI or Li). On the other hand, when an excess of phthalonitrile is absent, such a mechanism cannot operate; a reaction which *can* occur is the elimination of ammonia between two or more metal-free molecules of type (II; R = H), the condensation involving the imino- and the methyl group. Linstead and Rowe (*loc. cit.*) have shown that the imino-group of 3-iminophthalimidine can react with active methylene groups, and it is likely that the methyl group of (II; R = H) would be abnormally reactive, like that of α-picoline. Such a condensation, repeated thrice, would yield a four-unit intermediate which, by a further similar condensation, would cyclise to dehydrotetrabenzporphin. Experiment indeed shows that the reaction of an excess of methylmagnesium iodide with phthalonitrile yields a pigment with as many as three carbon links: the reason why one nitrogen link should persist is not clear, but may be due to the persistence of a little unchanged nitrile.

Another reaction of this type is the formation of tetrabenzmonazaporphin derivatives from the imino-acid (III) of Barrett and Linstead (*loc. cit.*), which is the dicarboxylic acid of the intermediate postulated in the Grignard reaction (or a double-bond isomeride of it). In this case, of course, elimination of carbon dioxide would also be required. The single aza-link may originate from phthalonitrile produced by pyrolysis of (III) into nitrile, acetic acid, and carbon dioxide. It should be noted that the aza-link is not always introduced, for the imino-acid and zinc acetate yield a considerable proportion of zinc tetrabenzporphin. In this connection, it is significant that the more stable 3-carboxymethylphthalimidine yields homogeneous tetrabenzporphins when fused with metals.

The compounds and methods described in this paper are being further investigated.

EXPERIMENTAL.

I. *Preparations from* 1-*Imino*-3-*dicarboxymethylenephthalimidine* (III)—An intimate mixture of 40 g. of the acid and 15 g. of zinc dust was heated, in about 2 g. portions, at 330—340° for

20 minutes. A deep green colour rapidly developed, and the mixture never became completely fused. Ammonia was freely evolved and a brilliant red liquid distilled into the cold part of the tube. The final product was a friable mass with a purple lustre. It was powdered and washed successively with dilute acid (to remove the excess of zinc), hot water, aqueous ammonia, and finally hot aqueous alcohol (10% water), which removed a large amount of red impurity. The residue was dried and dissolved in concentrated sulphuric acid. A current of hydrogen chloride was bubbled through the solution for ½ hour. The pigment was then precipitated by means of ice, collected, and washed with hot water, acetone, and alcohol in succession. The residue (8 g.) was thrice crystallised from chloronaphthalene, which yielded 6 g. of *tetrabenzmonazaporphin* (I, R = N) in green crystals with a bluish-purple lustre. Quinoline was a better crystallising medium, as one crystallisation gave pure material. A sample was also purified by sublimation, by the technique of Barrett, Dent, and Linstead (J., 1936, 1719), which yielded needles with a steely blue lustre. Tetrabenzmonazaporphin is slightly soluble in boiling quinoline and chloronaphthalene, very sparingly soluble in boiling pyridine, insoluble in the usual low-boiling solvents. The colour reactions are given in the Table on p. 1084 (Found for a typical sublimed sample: C, 82·0; H, 3·9; N, 14·3; Zn, nil. $C_{35}H_{21}N_5$ requires C, 82·2; H, 4·1; N, 13·7%). Samples which had been treated with sulphuric acid but without hydrogen chloride gave irregular analytical figures. If these were corrected for zinc content, the results were satisfactory. Even after treatment with hydrogen chloride on one occasion a product was obtained which left an ash, and there is therefore some uncertainty as to the exact conditions necessary for the complete elimination of the metal. The absorption spectrum * of the pure metal-free compound in the yellow to red region was :

	I.	II.	III.	IV.	V.	VI.
In quinoline	6900	6680	6380	6250	6100	6010 A.
In chloronaphthalene	6900	6690	6390	6250	6100	6000 A.

II > IV > I > III > V > VI

Another method of preparation is given on p. 1088.

For quantitative oxidation, approximately 50 mg. of the pigment were dissolved in concentrated sulphuric acid and precipitated with a large excess of ice. After the addition of 50 c.c. of N/10-ceric sulphate the mixture was heated for 30 minutes, and the excess of reagent estimated in the usual way (Dent, Linstead, and Lowe, *loc. cit.*). Results: 12·5, 12·6, 12·6, 12·4 g.-atoms of oxygen per molecule. By prolonging the period of heating to 90 minutes it was possible to raise this value to about 13·5 g.-atoms, but the results obtained during such long experiments were uncertain and there was a tendency for further oxidation (of the phthalimide formed). This had to be corrected for by blank experiments.

Conversion into metallic derivatives. 2 G. of the metal-free compound were heated with 1 g. of copper bronze for 12 hours in boiling quinoline (50 c.c.). The product was collected from the cooled solution and crystallised from chloronaphthalene, giving the pure copper derivative (1·5 g.) in needles with a blue-purple lustre. It resembled the parent compound in solubility. (Found : C, 73·4, 73·2; H, 3·3, 3·2; N, 12·0, 12·2; Cu, 10·8, 10·5. Found in a sublimed sample : C, 73·6; H, 3·35; N, 12·2; Cu, 11·5. Calc. : C, 73·3; H, 3·35; N, 12·2; Cu, 11·1%). Oxidation values were obtained by the method described above (Found : 12·5, 12·7, 12·5 g.-atoms of oxygen). The solution in concentrated sulphuric acid was grass-green. Addition of one drop of nitric acid turned this to dull greenish-blue, fading shortly to brown-red.

2 G. of the metal-free compound were boiled for 2 hours with 1 g. of anhydrous ferrous chloride in 30 c.c. of quinoline. The product was diluted with an equal volume of benzene, filtered from tar and ferrous chloride–quinoline complex, and poured into an excess of hydrochloric acid. The precipitated pigment was washed with aqueous ammonia, dried, and purified by sublimation. Ferrous tetrabenzmonazaporphin formed needles with a purple-blue lustre and a very dull green smear. It was insoluble in benzene, sparingly soluble in chloronaphthalene, acetone, and alcohol, but gave intensely bright green solutions in quinoline and pyridine. The brownish-green solution in sulphuric acid showed the usual colour change with nitric acid. The compound was precipitated unchanged from the sulphuric acid solution.

The metal-free compound (2 g.) was refluxed for 12 hours with magnesium powder (1 g.) in chloronaphthalene. The product was purified by sublimation, which yielded lustrous blue needles of the *magnesium* derivative. The sublimation was much more difficult than that of other derivatives of tetrabenzmonazaporphin. The compound was very soluble in chloro-

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* Routine measurements are given under the various preparations. The complete intensity data for pure compounds are collected on p. 1090.

naphthalene, quinoline, pyridine, acetone and alcohol, but insoluble in benzene. The solutions showed a magnificent red fluorescence, like those of other magnesium derivatives of macrocyclic pigments (Found: C, 78·4; H, 3·6; Mg, 4·8. $C_{35}H_{29}N_5Mg$ requires C, 78·8; H, 3·6; Mg, 4·6%). The magnesium was removable by boiling for 3 hours with dilute hydrochloric acid and also by the usual sulphuric acid treatment.

2 G. of the powdered metal-free compound were added to lithium ethoxide (1 g. of lithium in 80 c.c. of absolute alcohol). A deep green solution with a brilliant scarlet fluorescence was at once formed. After 6 hours' refluxing, 1·7 g. of metal-free compound remained undissolved. This was treated in exactly the same way with fresh lithium ethoxide and with the same result. The lithium derivative could not be isolated from the solution in a state of purity.

The zinc derivative was prepared from the metal-free compound, with zinc dust in boiling quinoline, in the same way as the copper compound.

Other fusions with the imino-acid. Reaction of the acid (40 g.) with anhydrous zinc acetate (10 g.) was carried out in exactly the same way as that with zinc dust, and the product was purified similarly. After removal of metal and crystallisation, 8·0 g. of benzazaporphin pigment were obtained (Found: C, 83·4; H, 4·0. Found, after sublimation: C, 83·2; H, 3·7; N, 13·2. Calc. for $C_{35}H_{21}N_5$: C, 82·2; H, 4·1; N, 13·7%. Calc. for $C_{36}H_{22}N_4$: C, 84·7; H, 4·35; N, 11·0%). The carbon analyses indicate the presence of about 40% of tetrabenzporphin. Quantitative oxidation under the conditions used for tetrabenzmonazaporphin gave rather irregular results, corresponding approximately to 13·5 g.-atoms of oxygen. Spectrum in chloronaphthalene:

I.	II.	III.	IV.	V.	VI.
6920	6680	6250	6180	6100	6020 A.

$\text{II} \gg \text{III} > \text{IV} > \text{I, V, VI.}$

The spectrum shows the presence of both tetrabenzmonaza- and tetrabenz-porphin. The 6180 band belongs to the latter, and the other bands of the triplet at 6100 and 6020 are sharper than in the spectrum of tetrabenzmonazaporphin.

In another experiment, the product of a similar fusion was washed with hot water and aqueous alcohol, crystallised from chloronaphthalene without removal of the zinc, and finally sublimed (Found: C, 73·7; H, 3·5; Zn, 11·4. Calc. for $C_{35}H_{19}N_5Zn$: C, 73·2; H, 3·3; Zn, 11·3%. Calc. for $C_{36}H_{20}N_4Zn$: C, 75·3; H, 3·5; Zn, 11·3%. These figures correspond to a monaza-content of some 75%). The spectrum corresponded fairly closely to that of the authentic zinc monaza-compound.

The imino-acid (20 g.) was fused with 8 g. of copper at 330—340°. The product was worked up in the usual way and purified through sulphuric acid and by crystallisation. Yield, 2 g. Spectrum in chloronaphthalene:

I.	II.	III.	IV.
6740	6460	6250	5970 A.

Although these maxima are almost identical with those of the monaza-derivative, the order of intensities is different: I>II>III>IV. The spectrum resembles closely that of "copper tetrabenzdiazaporphin" prepared by Helberger's method (see p. 1090. The material prepared by us by this method was not homogeneous. Helberger does not record the spectrum.) It is reasonably certain that the copper compound from the imino-acid contained at least a considerable porportion of the diaza-derivative.

Fusion of the imino-acid with either magnesium or magnesium acetate gave fair yields of benzazaporphin pigments which yielded metal-free pigments after treatment with sulphuric acid. Spectroscopic examination showed that these were mixtures. They await further investigation.

Fusion of mixtures of the imino-acid and phthalonitrile. (i) 23·2 G. of the imino-acid (2 mols.) were fused with 12·8 g. of phthalonitrile and 10 g. of zinc dust. (ii) 21 G. of the imino-acid (3 mols.) were fused with 3·9 g. of phthalonitrile and 8 g. of zinc dust. The products were purified in the usual manner and were finally treated with hydrogen chloride in sulphuric acid solution and crystallised. Yields: (i) 6·5 g., (ii) 4·2 g. [Found: (i) C, 76·2; H, 3·5; Zn, 4·9. (ii) C, 74·9; H, 3·7; Zn, 6·35%]. The incomplete removal of zinc clearly shows the presence of a nitrogenous pigment, either diaza- or higher. When allowance is made for the zinc content, the carbon figures correspond approximately to those of a diaza-compound.

The imino-acid (7 g.) was fused with 1·3 g. of phthalonitrile and 2 g. of copper bronze. The product (1·2 g.), purified as usual, was almost pure copper tetrabenztriazaporphin (Found : C, 69·3; H, 3·3; Cu, 11·0. Calc. for $C_{33}H_{17}N_7Cu$: C, 68·9; H, 3·0; Cu, 11·1%). Spectrum in chloronaphthalene : 6770, 6540, 6450, 6240, 5960 A. (cf. Barrett, Linstead, and Tuey, *loc. cit.*).

II. *Preparations from Phthalonitrile by the Grignard Reaction.*—(a) The Grignard reagent prepared from 6 g. of magnesium and 16 c.c. of methyl iodide (2·5 mols.) in ether was added to an ethereal suspension of powdered phthalonitrile (12·8 g.). The usual vigorous reaction ensued and a red-brown tar was formed. After an hour the ether was removed, the residue heated at 200°, and after 5 minutes steam blown through it; only a trace of organic material was thus removed. After an hour, the flask was allowed to cool somewhat, and hot dilute hydrochloric acid added. The dark blue residue was collected and washed with concentrated hydrochloric acid (1 part)–alcohol (3 parts) until the washings were only slightly coloured. The residue was dried, dissolved in sulphuric acid, and precipitated with ice. The tetrabenzmonazaporphin obtained was washed successively with hot dilute aqueous ammonia and alcohol, dried, and crystallised from chloronaphthalene. Yield, 2·2 g. (17%). The analytical sample was sublimed (Found : C, 82·3, 82·2; H, 4·1, 4·2; N, 13·5. Calc. for $C_{35}H_{21}N_5$: C, 82·2; H, 4·1; N, 13·7%). Spectrum in chloronaphthalene :

I.	II.	III.	IV.	V.	VI.
6950	6730	6410	6270	6130	5820 A.

II > IV > III, I, V > VI

The colour of a solution in sulphuric acid and the colour reaction with nitric acid were identical with those of the pigment prepared from the imino-acid.

In another experiment the initial reaction was carried out in the same way, but before the removal of the ether an additional amount (5 g.) of magnesium powder was throughly mixed with the product. The mixture was finally heated to 200° and treated with water. The resulting reaction tended to be violent, and to ignite the magnesium powder, hence it was advisable to work with an initial quantity of only 6·4 g. of phthalonitrile at a time. Only a very small yield of pigment was produced. The united product from ten such reactions was purified as before, passed through sulphuric acid, and crystallised from chloronaphthalene. 0·4 G. of crystalline monaza-compound was obtained (Found : C, 81·85; H, 4·35; N, 13·7%).

(b) *Experiments with* 1 : 1-*dimethyl*-3-*amino*-ψ-isoindole (IV). 5 G. of the crude base (Barrett, Linstead, and Tuey, *loc. cit.*) were refluxed for 2 hours with 20 c.c. of acetic anhydride. The product was poured into hot water and kept overnight. The brown solid was recrystallised from dilute alcohol (charcoal). 2-*Acetyl*-3 : 3-*dimethylphthalimidine* (V, R = $CO{\cdot}CH_3$) formed colourless needles (3 g.), m. p. 105—106° (Found : C, 70·6; H, 6·2; N, 7·1. $C_{12}H_{13}O_2N$ requires C, 70·9; H, 6·4; N, 6·9%). 2·4 G. of the acetyl compound were hydrolysed on the steam-bath with 10 c.c. of concentrated hydrochloric acid and 10 c.c. of water for 4 hours. The product was diluted with an equal bulk of water and kept overnight. Yield, 1·5 g. of 3 : 3-*dimethylphthalimidine* (V, R = H), which formed long colourless needles from dilute alcohol, m. p. 162° (Found : C, 74·3; H, 7·1; N, 8·7. $C_{10}H_{11}ON$ requires C, 74·5; H, 6·8; N, 8·7%).

In attempts to synthesise the last compound, dimethylphthalide was prepared by Bauer's method (*Ber.*, 1904, **37**, 735). It crystallised from benzene–petrol in large cubic crystals, m. p. 72°. Bauer gives m. p. 67°. It resisted the action of ammonia under the following conditions : Treatment of the molten substance with gaseous ammonia, either alone or in the presence of zinc chloride; treatment of the substance during 4 weeks at 0° with alcoholic ammonia.

1 : 1-Dimethyl-3-amino-ψ-*iso*indole, when fused with zinc acetate at 350° in the usual way, gave only a very small amount of a benzazaporphin; 3 : 3-dimethylphthalimidine, identified by m. p. and mixed m. p. (162°), condensed on the cool walls of the tube. Better results were obtained as follows : 2 G. of the base were mixed with 1 g. of anhydrous zinc acetate. The mixture was placed in four tubes, which were heated rapidly in a naked flame. A purple vapour giving a crimson condensate was evolved and at this stage the reaction was continued in an electrical heater at such a rate that the red liquid refluxed quietly. After about 45 minutes, the red colour faded and no further pigment appeared to be produced. The product was extracted in 30 c.c. of hot pyridine, the solution cooled, diluted with 100 c.c. of ether, filtered from black material, and passed through a column of alumina (30 × 2 cm.), which removed brown impurities, it was then concentrated to *ca.* 10 c.c. and again diluted with 100 c.c. of ether.

Violet crystals separated overnight (Found : C, 74·75; H, 3·9; Zn, 9·6. $C_{35}H_{19}N_5Zn$ requires C, 73·1; H, 3·3; Zn, 11·4%). Spectrum (in pyridine–ether) :

I.	II.	III.	IV.	V.	VI.
6650	6410	6230	5690	4610	4320 A.

VI > III > II > I > IV, V

The two strongest absorption bands and the high carbon content both indicate the presence of zinc tetrabenzporphin, and some removal of metal is shown by the low zinc content.

III. *Preparations from* 3-*Carboxymethylphthalimidine.*—The acid was prepared by methods described in Part XVII (this vol., p. 1072) and was in the " anhydrous ", *i.e.* cyclic, form.

A mixture of 2 g. of the acid and 1 g. of zinc dust was poured into a tube, pre-heated to 320°, and maintained at this temperature during 4 hours while nitrogen was passed through it. Water and a gas (presumably carbon dioxide) were evolved during the early stages, and an intensely purple condensate formed on the cool parts of the tube. The melt was finally cooled and dissolved in pyridine (35 c.c.), and the solution diluted with ether, filtered from a black precipitate, evaporated to small bulk, and diluted with methanol. (This convenient method of working up the product follows that used by Helberger in the preparation of zinc tetrabenzporphin from methylphthalimidine.) The yield of crystalline zinc pigment was 0·51 g. Similar yields (about 30%) were obtained on a larger scale. A comparative experiment on the fusion of methylphthalimidine (2 g.) with zinc acetate (Helberger and Hevér, *loc. cit.*) gave 0·27 g. of an identical product. It is probable, however, that neither of these substances was quite pure and that the recorded yields are too high. This point is being further investigated.

Zinc tetrabenzporphin, purified by crystallisation from chloronaphthalene or by sublimation, formed fine needles with a blue reflex (Found : C, 75·6; H, 3·7; N, 10·1; Zn, 11·2. Calc. for $C_{36}H_{20}N_4Zn$: C, 75·3; H, 3·5; N, 9·8; Zn, 11·4%). Another preparation by the same method had suffered a slight removal of metal (Found : C, 76·6; H, 3·8; Zn, 10·2%). The analytically pure material gave a green solution in hot pyridine with a weak reddish-brown fluorescence. Zinc tetrabenzporphin dissolved in sulphuric acid to give a green solution, which, after hydrogen chloride had been bubbled through it for 1 hour, was filtered and poured on ice. The precipitated tetrabenzporphin was washed free from acid, dried, crystallised from chloronaphthalene and sublimed; it formed long, steel-blue needles (Found for two separate preparations: C, 84·6, 84·9; H, 4·2, 4·2; N, 11·1. Calc. for $C_{36}H_{22}N_4$: C, 84·7; H, 4·35; N, 11·0%). When the zinc pigment was treated with sulphuric acid without hydrogen chloride, the tetrabenzporphin left an ash of 2·5% (zinc oxide). The metal-free pigment could be prepared directly from the crude product of the fusion of 3-carboxymethylphthalimidine and zinc as follows : The melt was powdered and extracted exhaustively with hot concentrated hydrochloric acid–alcohol (1 : 3). The residue was dried, treated with hydrogen chloride and sulphuric acid, and purified as before.

Quantitative oxidations. About 15 mg. of the compound were dissolved in 5—10 c.c. of concentrated sulphuric acid and precipitated by ice. 50 C.c. of N/10-ceric sulphate were added, and the mixture heated at 100° for 40 minutes. The solution was cooled, and the excess of ceric sulphate estimated as usual (Found for metal-free tetrabenzporphin : 16·2, 16·3, 16·1 g.-atoms of oxygen; for the zinc derivative : 17·3, 16·85, 17·3 g.-atoms).

The carbon dioxide evolution was estimated by the method used by Barrett, Linstead, and Tuey (*loc. cit.*) for tetrabenztriazaporphin. About 50 mg. of the pigment, dispersed as usual, were oxidised by means of 75 c.c. of N/10-ceric sulphate diluted with 50 c.c. of water, and the carbon dioxide led by means of a stream of nitrogen into N/10-baryta. The excess of baryta was titrated, and the excess of ceric sulphate determined in the usual way. Zinc tetrabenzporphin took up 17·3 g.-atoms of oxygen and yielded 3·97 mols. of carbon dioxide. The oxidation of the metal-free pigment was incomplete under the same conditions.

Other metallic derivatives of tetrabenzporphin. The copper derivative was made following the method of Helberger and Hevér (*Annalen*, 1938, **536**, 173) from tetrabenzporphin and cuprous chloride in quinoline (Found for sublimed material : C, 75·3; H, 4·0; Cu, 11·0. Calc. for $C_{36}H_{20}N_4Cu$: C, 75·5; H, 3·5; Cu, 11·2%). Ferrous tetrabenzporphin was similarly prepared (using ferrous chloride) and purified by sublimation.

Magnesium tetrabenzporphin was prepared by heating 3-carboxymethylphthalimidine (2 g.) with 1 g. of magnesium powder at 320° for 4 hours. The usual formation of water and a purple condensate occurred. The pigment was isolated by the method already described for the zinc compound. As there was more contamination by tarry impurities, the pyridine–ether solution (after filtration) was percolated through a column of alumina before the pigment was crystallised.

The yield of crystalline material was variable and lower than that obtained by the use of zinc. The pigment crystallised from chloronaphthalene–methanol in a solvated form. This agrees with Helberger, von Rebay, and Hevér (*loc. cit.*), who prepared the same compound from methylphthalimidine and crystallised it from pyridine–methanol or acetone–methanol. They considered it to be a monohydrate. Alternatively it is possible that it may contain one molecule of methanol [Found (present work) : C, 78·3; H, 3·9; N, 9·6; Mg, 4·75. Found (Helberger *et al.*) : C, 78·9; H, 4·0; N, 10·0; Mg, 5·5; O, 3·1. Calc. for $C_{36}H_{20}N_4Mg,H_2O$: C, 78·5; H, 4·0; N, 10·2; Mg, 4·4; O, 2·9%. Calc. for $C_{36}H_{20}N_4Mg,CH_4O$: C, 78·7; H, 4·3; N, 9·9; Mg, 4·3; O, 2·8%]. After sublimation the unsolvated *magnesium* derivative was obtained (Found : C, 80·7; H, 3·8; Mg, 4·8. $C_{36}H_{20}N_4Mg$ requires C, 81·2; H, 3·8; Mg, 4·5%).

IV. *Preparations from* o-*Cyanoacetophenone*.—The preparation of *o*-cyanoacetophenone from *o*-bromoacetophenone and cuprous cyanide in pyridine (Helberger and von Rebay, *loc. cit.*) was inconvenient owing to difficulties due to tar formation and gave variable yields. The following method was adopted : A solution of 10 g. of *o*-bromoacetophenone, 0·5 g. of iodine, and 5 g. of cuprous cyanide in 40 c.c. of phenylacetonitrile was stirred at 108—112° for 5½ hours, cooled somewhat, and poured into 600 c.c. of ether. The tarry layer was extracted with ether and then with acetone. The original ethereal solution and the extracts were concentrated and the united residue was distilled from a flask with a wide side-arm. After the removal of phenylacetonitrile (b. p. 103—106°/10 mm.), the cyanoacetophenone distilled at 148—150°/10 mm. and at once solidified. Yield 4·2 g.; m. p. 48°; semicarbazone, m. p. 219°.

Copper tetrabenzmonazaporphin was prepared from the cyano-ketone (2 g.), following Helberger and von Rebay, and was crystallised from pyridine and then from chloronaphthalene. Yield, 0·12 g. (Found after sublimation : C, 73·0; H, 3·3; N, 12·6; Cu, 11·7. Calc. for $C_{35}H_{19}N_5Cu$: C, 73·3; H, 3·35; N, 12·2; Cu, 11·1%). Spectrum in chloronaphthalene :

I.	II.	III.	IV.
6750	6470	6290	6020 A.; II = III > I > IV

By the method used by Helberger for the preparation of copper tetrabenzdiazaporphin, 1·0 g. of cyanoacetophenone, 0·5 g. of phthalonitrile, 0·6 g. of cuprous chloride, and 4 c.c. of quinoline yielded a pigment which was only partly soluble in boiling pyridine. The solution had the following spectrum in pyridine :

I.	II.	III.	IV.
6720	6460	6220	5950 A.; I > II > III > IV.

The portion insoluble in pyridine was extracted with boiling chloronaphthalene, and the crystalline material sublimed (Found : C, 69·9; H, 3·0; N, 15·9; Cu, 11·5. Calc. for an equimolecular mixture of copper tetrabenz-diaza- and -triaza-porphin : C, 70·0; H, 3·1; N, 15·85; Cu, 11·1%). The spectrum was similar to that given above, but band IV was more intense than band III.

V. *Absorption Spectra.*—Intensity measurements were carried out with a Hilger–Nutting spectrophotometer with a Pointolite lamp as the source of light. Solutions of pigments were prepared by dissolving an accurately weighed amount (about 1 mg.) either (i) in 20—30 c.c. of freshly distilled chloronaphthalene, boiling for a few minutes, cooling, and diluting to 100 c.c., or (ii) in 15—20 c.c. of warm pyridine, cooling, and diluting to 100 c.c. with ether. Owing to the sparing solubility of the pigments there was always some doubt as to whether complete solution had been obtained prior to the measurements. Accordingly after about 5 days the solutions were again boiled for a few minutes and cooled, and the spectra re-examined. Agreement of the two sets of results indicated that no undissolved pigment was present during either measurement. The intensities of the bands of certain solutions decreased on standing in a manner which has already been described. The intensity measurements in such cases obviously have little quantitative significance and are not given numerically.

A 2 cm. tube was always used. For the measurement of the strongest bands, it was necessary to dilute the solutions, prepared as described above, four or even eight times. The intensity measurements in the blue and violet are less accurate than those in the orange and red regions.

Intensity results are expressed in the usual way as logarithms of the molecular extinction coefficients.

Results (these should be compared with the data already given for control purposes in the preparative work).

Tetrabenzmonazaporphin, from imino-acid (chloronaphthalene).

$\lambda_{max.}$	6900	6690	6390	6260	6100	4390	4240 A.
log $\epsilon_{max.}$ ...	4·45	4·72	4·34	4·57	4·40	4·87	4·89

There are also weak bands at 6010 and 5830 A

Copper tetrabenzmonazaporphin (chloronaphthalene).

$\lambda_{max.}$	6780	6510	6300	5980	5740	4620	4220 A.
log $\epsilon_{max.}$ ...	4·17	5·01	4·89	4·25	4·11	3·75	4·93

Zinc tetrabenzmonazaporphin (chloronaphthalene).

$\lambda_{max.}$	7020	6760	6510	6330	6070	5900	5770	4570	4350 A.
Intensity	weak	medium	medium	high	weak	weak	weak	medium	v. high

(pyridine–ether)

$\lambda_{max.}$	6630	6400	6240	6120	5900	5830	5710	4240	4140 A.
log $\epsilon_{max.}$ ...	4·72	5·19	4·98	4·32	4·18	4·15	4·08	5·29	5·18

and weaker bands at 5650 and 4540 A.

Magnesium tetrabenzmonazaporphin (pyridine–ether).

$\lambda_{max.}$	6680	6450	6290	6170	6010	5920	5820	5750	4320	4210 A.
log $\epsilon_{max.}$ ...	4·53	5·28	5·02	4·30	4·28	4·26	4·23	4·11	5·15	5·34

Ferrous tetrabenzmonazaporphin (pyridine–ether).

$\lambda_{max.}$	6440	6180	5980	4270 A.
log $\epsilon_{max.}$ ...	4·26	4·68	4·78	4·92

Helberger and co-workers gave for the spectrum of this compound in pyridine–ether : I, 6220; II, 6040; III, 5750; IV, 5550; end absorption, 4365 A. Bands I and II roughly correspond with two observed by us, and the end absorption corresponds with the intense band at 4270 A. The weaker bands, 5750, 5550, observed by Helberger may perhaps be due to the presence of ferrous tetrabenzporphin (*q.v.*).

Tetrabenzporphin (from 3-carboxymethylphthalimidine) (chloronaphthalene).

$\lambda_{max.}$	6680	6210	6120	6040	5900	5760	5660	4380	4220 A.
log $\epsilon_{max.}$ ...	4·80	4·90	4·90	4·80	4·21	4·25	4·22	5·34	5·21

The first four bands, which are easily measured visually, correspond closely with those observed (in pyridine solution) in our preparative work and (in quinoline solution) by Helberger.

Copper tetrabenzporphin (chloronaphthalene).

$\lambda_{max.}$	6700	6280	6120	6040	5780	4260 A.
log $\epsilon_{max.}$ ...	4·50	5·22	4·71	4·63	4·33	5·40

Helberger and Hevér (*Annalen*, 1938, **536**, 173) found (in pyridine–ether) two bands at 6230 and 4290 A. corresponding with the two dominant bands above.

Zinc tetrabenzporphin (pyridine–ether).

$\lambda_{max.}$	6540	6320	6060	5900	5780	4580	4360	4260	4110 A.
log $\epsilon_{max.}$ ...	4·02	5·18	4·08	4·34	4·26	4·57	5·82	5·42	4·88

Magnesium tetrabenzporphin (pyridine–ether).

$\lambda_{max.}$	6540	6320	6060	5890	5790	4580	4360	4250	4110 A.
log $\epsilon_{max.}$ ...	3·79	5·07	3·81	4·23	4·11	4·49	5·76	5·00	4·77

Ferrous tetrabenzporphin (pyridine–ether).

$\lambda_{max.}$ ...	5960	5740	5500	4280 A.
log $\epsilon_{max.}$ ...	4·88	4·30	4·11	5·04

(chloronaphthalene).

$\lambda_{max.}$	6190	5760	5480 A.
log $\epsilon_{max.}$.. ...	4·78	4·15	4·23

Phthalocyanine derivatives.

Substance.	Solvent.							
Metal-free	Chloronaphthalene	$\lambda_{max.}$	7030	6680	6360	6040	5760	5560 A.
		log $\epsilon_{max.}$	5·23	5·22	4·75	4·52	4·02	3·88
Copper	,,	$\lambda_{max.}$	6830	6480	6120	5820	5640 A.	
		log $\epsilon_{max.}$	5·36	4·70	4·77	4·11	4·00	
Zinc	,,	$\lambda_{max.}$	6810	6490	6110 A.	and weaker bands.		
		log $\epsilon_{max.}$	5·35	4·48	4·54			
Magnesium	,,	$\lambda_{max.}$	7020	6800	6480	6110 (fading) A.		
		log $\epsilon_{max.}$	4·15	4·93	4·08	4·08		
Ferrous	,,	$\lambda_{max.}$	6580	6320	5970		(fading) A.	
		log $\epsilon_{max.}$	4·70	4·26	4·20			
,,	Pyridine–ether	$\lambda_{max.}$	6490	6230	5900		(fading) A.	
		log $\epsilon_{max.}$	5·01	4·46	4·43			

Tetrabenztriazaporphin derivatives.

Substance.	Solvent.								
Metal-free	Chloronaphthalene	$\lambda_{max.}$	6940	6520	6380	6220	5920	5700	4620 A.
		log $\epsilon_{max.}$	5·19	5·03	4·75	4·66	4·43	4·03	4·03
Copper	,,	$\lambda_{max.}$	6840	6550	6270	6140	6000	4460 A.	
		log $\epsilon_{max.}$	5·21	5·01	4·58	4·57	4·49	3·85	
Zinc	,,	$\lambda_{max.}$	6780	6540	6260	6130	5980	4440	4265 A.
		log $\epsilon_{max.}$	5·23	5·00	4·43	4·42	4·38	4·20	4·51
Magnesium	,,	$\lambda_{max.}$	7220	6810	6580	6300	6150	6000	4480 A.
		log $\epsilon_{max.}$	4·36	4·96	4·82	4·30	4·38	4·18	4·18
Ferrous	,,	$\lambda_{max.}$	6570	6350	5820 A.				
		log $\epsilon_{max.}$	4·74	4·67	4·23				
,,	Pyridine–ether	$\lambda_{max.}$	6460	6250	5920	5710 A.			
		log $\epsilon_{max.}$	4·98	4·83	4·46	4·36			

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