

581. *Phthalocyanines and Related Compounds. Part XX. Further Investigations on Tetrabenzporphin and Allied Substances.**

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The paper describes: (i) The preparation and purification of tetrabenzporphin (II). (ii) The sulphonation of phthalocyanine and other macrocyclic pigments: it is shown that the sulphonated pigments are more easily oxidised than the parent substances; the sulphonation of phthalocyanine occurs in the 4-position. (iii) The halogenation of tetrabenzporphin: as in the case of phthalocyanine, both addition and substitution of halogen can be realised.

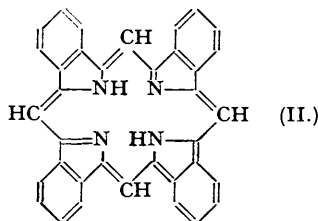
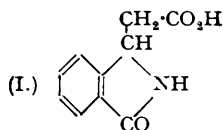
(i) *Preparation of Tetrabenzporphin and its Zinc Compound.*—We have examined further the two methods already used, namely, the reaction between methylphthalimidine and zinc acetate (Helberger and Hevér, *Annalen*, 1938, **536**, 173) and that between 3-carboxymethylphthalimidine (I) and zinc acetate (Barrett, Linstead, Rundall, and Tuey, *J.*, 1940, 1079). We have also examined certain related reactions, namely, those between the same acid (I) and metallic zinc or zinc chloride, and those between the amide of the acid and metallic zinc or zinc acetate. In all these, zinc tetrabenzporphin was produced. The product could be assayed spectroscopically, the intensity of the band in the red with maximum at 6320 Å. being used to give a measure of the content of zinc tetrabenzporphin. Zinc tetrabenzporphin is among the most highly coloured of organic compounds; at this wave-length the intensity has a value for $\log_{10} \epsilon$ of 5.18. The detailed results are given in the experimental section (Tables I and II). The best method for routine preparations was that which we had used previously—reaction between the acid and zinc acetate—both because the yield of pigment was highest and because the intermediate acid was readily accessible from β -naphthol.

Zinc tetrabenzporphin is only formed from the acid at a bath-temperature above 320° (corr.). Over the range 345—420° pigment formation occurs and temperature has little effect on the yield. The pigment is still formed in considerable yield at as high a temperature as 510°.

Intensely green crystalline material with a purple reflex can be isolated from the product without great difficulty by the method used by Helberger and in our previous work. Spectroscopic examination, however, showed that this was of variable and unsatisfactory purity.

* The work described in this and the following paper was carried out during the years 1939—41 in the Converse Memorial Laboratory of Harvard University (Weiss, Ph.D. Thesis, Harvard, 1941).

Further purification could not be effected either by crystallisation or by chromatography because the impurities had solubilities similar to the desired zinc tetrabenzporphin and were



similarly adsorbed. The zinc pigment could be isolated in the pure state by sublimation, but this was not a convenient procedure for any appreciable quantity. Finally, the following rather unorthodox method was devised: it was observed that during the process of sublimation the impurities were converted into a coke-like material which was no longer soluble in pyridine. Accordingly, for the final purification the crude zinc tetrabenzporphin was heated to 450° in an atmosphere of nitrogen without sublimation. The zinc tetrabenzporphin, which was substantially unchanged, was then extracted with pyridine and the solution filtered through an alumina column. The pigment was precipitated in beautiful crystals by the addition of methanol to the pyridine eluate, followed by evaporation. The best yield of pure zinc tetrabenzporphin was 15.5%, and yields of 13% could regularly be obtained.

In agreement with our previous paper (*loc. cit.*), the zinc pigment gave pure metal-free tetrabenzporphin (II) by treatment of its solution in sulphuric acid with hydrogen chloride followed by vacuum sublimation, but not by treatment with sulphuric acid alone.

We explored a different and more speculative method for the preparation of tetrabenzporphin but without success. It will be recalled that phthalonitrile reacts readily with sodium amyloxide to give disodium phthalocyanine (Barrett, Dent, and Linstead, *J.*, 1936, 1720). The reaction may proceed through a chain mechanism involving the intermediate formation of a metallic "cyanyl" radical corresponding to Schlenk's ketyls (Barrett, Linstead, and Tuey, *J.*, 1939, 1812). We therefore examined the action of sodium amyloxide on methyl *o*-cyanocinnamate in the hope that this might yield a tetrabenzporphin derivative by an analogous process involving the formation of methin links. A deep-green solution was in fact formed, but when heated this became brown and gave only tarry material. Neither were we able to involve methyl *o*-cyanocinnamate residues in the growing of a chain of phthalonitrile units. When a mixture of the cyano-ester and the nitrile was heated with sodium amyloxide it gave pure disodium phthalocyanine, no methin links being formed.

(ii) *Sulphonation of Various Macrocyclic Pigments.*—The conversion of phthalocyanine into intensely coloured sulphonated derivatives soluble in water and alkali has been investigated in industrial research laboratories (see, *e.g.*, B.P. 457,796, 460,147, I.G. Farbenind.; and U.S.P. 2,150,741, Imperial Chemical Industries). We have made a preliminary comparative study of the sulphonation of macrocyclic pigments with the following results. Sulphonation of metal-free phthalocyanine was conveniently effected with 30% oleum at 80°: the product contained between 3 and 4 sulphonic groups. When the molecule contained methin links in place of nitrogen atoms, the overall resistance to fuming sulphuric acid was lowered, but it was still possible to bring about substitution in the benzene rings under suitable conditions. For example, metal-free tetrabenzporphin (Barrett, Linstead, and Tuey, *loc. cit.*) underwent gross decomposition on treatment with 30% oleum even at room temperature, but 15% oleum converted it into a mixture of sulphonic acids soluble in water and alkali. The product contained an average of between 1 and 2 sulphonic groups per molecule. Zinc tetrabenzporphin was converted into a green alkali-soluble pigment by 30% oleum at room temperature without gross decomposition. The absorption spectra of these sulphonated derivatives are much more diffuse than those of the parent compounds.

The most characteristic property of the sulphonic acids is their ease of oxidation. The unsulphonated pigments have an appreciable resistance towards oxidation. Thus phthalocyanine is converted into an intermediate oxidation product in which the great ring is preserved and which has an appreciable stability towards an excess of oxidizing agent. The stability is more marked with the less-nitrogenous pigments (see following paper). On the other hand, phthalocyaninesulphonic acid, on treatment with ceric sulphate at room temperature, passes through the intermediate state of oxidation in less than a second. The uptake of oxygen is one

atom per molecule, as in the case of the unsulphonated pigment (Dent, Linstead, and Lowe, *J.*, 1934, 1033).

Tetrabenztriazaporphinsulphonic acid also is more susceptible to oxidation than is the parent substance. There is an indication that if a mixture of pigments containing different proportions of nitrogen and methin links is sulphonated, there is a concentration of nitrogen-linked material in the sulphonated product, *i.e.*, sulphonation is accompanied by some selective decomposition of methin-linked pigment. Thus a pigment, substantially tetrabenztriazaporphin, with an oxygen uptake of 4.5 atoms per molecule, was sulphonated to an acid with an oxygen uptake of only 4 atoms per molecule.

Sulphonation of phthalocyanine occurs in the 4-position of the benzene rings, although this may not be the only position attacked. Fission of a sulphonated pigment yielded phthalimide and 4-sulphophthalimide. The latter was oriented by conversion into 4-hydroxyphthalic acid, identified as its crystalline dimethyl ester. This orientation of the sulphonated pigment is also supported by the fact that its fusion with alkali yielded *p*-hydroxybenzoic acid. The sulphonation thus resembles halogenation (Barrett, Bradbrook, Dent, and Linstead, *J.*, 1939, 1820) in occurring preferentially in the β -positions of the aromatic rings.

A sulphonated copper phthalocyanine has been made by heating 4-sulphophthalic anhydride with urea and copper salts (I.C.I., F.P. 807,052). This material differs from that made by direct sulphonation of copper phthalocyanine in having a redder shade of blue. This suggests that the direct sulphonation of the copper pigment goes to some extent in the 3-position (see Haddock, *J. Soc. Dyers Col.*, 1945, 61, 71). It is conceivable that some 3-sulphonated material may have been degraded in our oxidation procedure. It is also possible that the lack of symmetry of the direct sulphonation product affects its colour.

We examined the possibility of converting phthalocyaninesulphonic acid into hydroxyphthalocyanine by potash fusion but without success; nor did it seem possible to regenerate phthalocyanine by removal of the sulphonic group by acid hydrolysis.

(iii) *Halogenation of Tetrabenzporphin.*—Phthalocyanine is known to react with halogens under mild conditions to give additive compounds. At high temperatures, and in the presence of catalysts nuclear substitution occurs (Barrett, Bradbrook, Dent, and Linstead, *loc. cit.*). We found that halogenation of the tetrabenzporphin ring follows much the same course. Zinc tetrabenzporphin reacted rapidly at room temperature with bromine in carbon tetrachloride. The maximum uptake of halogen was 7.1 atoms per molecule, nearly all of which was lost by treatment with cold dilute alkali. Nuclear bromination was best achieved by heating zinc tetrabenzporphin with bromine and phosphorus tribromide at 250°. The bromo-derivative was obtained as a black powder, giving a brownish-yellow solution in pyridine. Analysis indicated a bromine content of 17.5 atoms per molecule. The bromo-compound underwent gross decomposition when its pyridine solution was boiled.

Chlorination was conveniently achieved by the action of a mixture of thionyl chloride and sulphuryl chloride at the boiling point. The products isolated contained from 9 to 11 atoms of chlorine per molecule. They were dark powders with a dull green reflex and gave brown-yellow solutions in pyridine. In a number of experiments, using conditions under which phthalocyanine gives good yields of highly halogenated pigments, we found that zinc tetrabenzporphin was decomposed. These results are summarised in the experimental portion. We attribute the comparative instability of the tetrabenzporphin ring towards halogenating agents to the instability of compounds substituted on the linking (*meso*) carbon atoms. It is interesting to compare these results with those of Hans Fischer on the halogenation of porphyrins [summarised in Fischer and Orth, "Die Chemie des Pyrrols," Vol. II, (1), p. 230]. He found that the *meso*-positions were readily substituted by halogen. The products lost halogen on treatment with base and regenerated the parent compound in two steps.

EXPERIMENTAL.

(i) *Preparation of Tetrabenzporphins.*

Intermediates.—In the routine preparation of carboxymethylphthalimidine [*iso*indolinone-3-acetic acid (I)] the yield of *o*-cyanocinnamic acid from 1-nitroso-2-naphthol was 73%, and that of carboxymethylphthalimidine from the cyano-acid was 88%. *iso*Indolinone-3-acetamide, prepared following Rowe, Haigh, and Peters (*J.*, 1936, 1101), melted at 218–219° (lit. 221°). The zinc salt was obtained by dissolving 12 g. of the acid in aqueous sodium hydroxide, neutralising (phenolphthalein) with *N*/10-hydrochloric acid, and adding an aqueous solution of 7.3 g. (1.05 moles) of zinc acetate dihydrate. When the solution was heated (steam-bath) for 15 minutes a heavy precipitate separated. After a further hour at room temperature, the solid zinc salt was removed by filtration and freed from any parent acid by extraction with 100 c.c. of hot alcohol. The salt, which was insoluble in alcohol, was crystallised from

3 l. of hot water. 11 g. (75%) of white needles of zinc isoindolinone-3-acetate were so obtained, m. p. 189—190° (decomp.) (Found: N, 6.1. $C_{20}H_{16}O_6N_2Zn$ requires N, 6.3%).

Methyl o-cyanocinnamate was prepared from the acid by the Fischer-Speier method or by the use of diazomethane. It crystallized from water in white needles, m. p. 60° (Found: MeO, 16.6. $C_{11}H_9O_2N$ requires MeO, 16.6%). The ethyl ester melted at 75°. The methyl ester gave a deep green colour when it was added to a hot solution of sodium amyloxide, but no product could be isolated from the solution. A mixture of the methyl ester (100 mg.) and phthalonitrile (10 mg.) was added to a solution of sodium amyloxide in amyl alcohol, and the mixture boiled for 3 hours under reflux. The solid produced (10 mg.) was blue with a red reflex. It was purified *via* solution in sulphuric acid in the usual way and was identified as phthalocyanine spectroscopically. No macrocyclic pigment could be detected when methyl *o*-cyanocinnamate was treated with methylmagnesium iodide under conditions which convert phthalonitrile into tetrabenztriporphin (Barrett, Linstead, and Tuey, *loc. cit.*).

Preparation of Zinc Tetrabenzporphyrin.—The best method is given below. Other processes are summarised in Tables I and II. The preferred method is an improvement of the process of Barrett, Linstead, Rundall, and Tuey (*loc. cit.*): Ten test tubes (3 × 20 cm.), supported upright, were preheated to 340—345° by a bath of Wood's metal, overlaid by charcoal. Nitrogen was passed through the tubes, and into each was added an intimate mixture of carboxymethylphthalimidine (3.5 g.) and zinc acetate dihydrate (2.6 g.), heating being continued for 3.5 hours. The ten products were cooled, united, and dissolved in hot pyridine (800 c.c.). The deep-green solution was poured into ether (3 l.), filtered, and evaporated to 50 c.c. A litre of methanol was then added, which precipitated crude zinc tetrabenzporphyrin (7.5 g.). This was assayed spectroscopically, by using the band of λ 6320 Å.; $\log_{10} \epsilon$ 5.18 (Barrett, Rundall, Linstead, and Tuey, *loc. cit.*). It contained 4.8 g. of zinc tetrabenzporphyrin (18% yield).

For purification, the zinc pigment was placed on one side of a filter-plate and glass wool plug located half-way down a horizontal tube of Pyrex glass (3 × 40 cm.) through which nitrogen was passed. The tube was held in an asbestos sleeve in an iron pipe, and heated at 450° for 30 minutes. During this time pyridine and a brown oil collected at the cold exit end of the tube, and other impurities in the pigment were carbonized. 10 g. of crude pigment, assaying 6.8 g. of zinc tetrabenzporphyrin, were thus heated. The residue was cooled and extracted with pyridine (1 l.), which was then passed through a column (18 × 3 cm.) made up of equal parts of alumina and diatomaceous earth; elution with a further 100 c.c. of pyridine left a brown layer at the top. The united pyridine eluate on concentration to small bulk and dilution with methanol gave 6.5 g. of platelets with a beautiful purple lustre. This material is pure zinc tetrabenzporphyrin except that it contains about 0.7 mol. of pyridine per mol. of pigment (299 mg. after 4 hours at 130°/2 mm. had lost 26 mg. of pyridine) (Found, for solvent-free pigment: C, 75.3; H, 3.7; Zn, 10.9. Calc. for $C_{36}H_{20}N_4Zn$: C, 75.3; H, 3.5; Zn, 11.4%). Zinc tetrabenzporphyrin could be sublimed at atmospheric pressure in the apparatus described below to give beautiful needles, some 1 cm. long, with a purple-blue reflex.

The temperature used in the carbonisation process and quoted above (450°) seems to be about the optimum. A series of comparative experiments was carried out in which samples of crude zinc tetrabenzporphyrin were heated to different temperatures; the products were extracted as described above and the zinc tetrabenzporphyrin assayed spectroscopically. The recoveries corresponding to various "coking" temperatures were: 450°, 86%; 480°, 76%; 520°, 50%. Crude products containing as little as 10% of zinc tetrabenzporphyrin have been purified by this process.

Preparation of Tetrabenzporphyrin.—1.6 g. of the pure zinc compound were dissolved with stirring in 125 c.c. of cold concentrated sulphuric acid. Hydrogen chloride was bubbled through the solution at 0° for 1 hour, after which it was filtered on to 300 g. of crushed ice made from distilled water. The product was neutralised with aqueous ammonia (which helps to coagulate the precipitate), reacidified with sulphuric acid, and filtered hot. The purple-blue precipitate was washed with hot water until free from sulphate, and then with alcohol, and dried, the yield being 1.1 g. (75%).

TABLE I.

Effect of conditions on the yield of zinc tetrabenzporphyrin from carboxymethylphthalimidine and zinc acetate.

Expt. no.	Bath temp. (corr.).	Time of reaction, hrs.	Yield, %.	Expt. no.	Bath temp. (corr.).	Time of reaction, hrs.	Yield, %.	Expt. no.	Bath temp. (corr.).	Time of reaction, hrs.	Yield, %.
1 *	340—345°	3.5	18	6	350	4	15	12	510	0.5	9
2	320	2	0.5	7	355	4	17	13	350	0.75	6
3	330	4	12	8	373	3½	15	14	350	1.6	10
4 †	330	4	13	9	390	3	15	15	350	3	11
5	345	4	15	10	420	2	15	16	350	5	11
				11	450	1	10				

* Optimum conditions.

† Anhydrous zinc acetate was used in this experiment.

This material contained a small amount of zinc which could be removed by sublimation. This was done in a Pyrex tube (No. 172; 12 × 340 mm.), in the middle of which a filter-plate and glass-wool plug were held against indentations. Crude tetrabenzporphyrin (200 mg.) was introduced behind the plug, the pressure was reduced to 2 mm., a slow stream of nitrogen (2 bubbles/sec.) was passed through, and the tube was heated immediately below the sample. Beautiful purple-blue crystals of tetrabenzporphyrin collected about 5 cm. past the plate; further on there was a zone of brown oil. At the end of the

sublimation the oil was removed with a pad of cotton wet with methanol; the tetrabenzporphin (110 mg.) could then be tapped from the tube (Found : C, 84.6; H, 4.3; no residue. Calc. for $C_{36}H_{22}N_4$: C, 84.7; H, 4.4%).

Other Methods for the Preparation of Zinc Tetrabenzporphin.—Table I summarises the results obtained by the use of other conditions for the preparation of zinc tetrabenzporphin from zinc acetate and carboxymethylphthalimidine. The temperature is important at the lower end of the scale. Thus, below 330° the yield falls off (Experiment 2) but the range can be extended upwards from 350° with but little decrease in efficiency (Expts. 7—12). The effect of time of reaction is indicated in the four parallel experiments, 13—16. The optimum conditions, already described in detail, are included as Expt. 1 for comparison. The zinc tetrabenzporphin was estimated spectroscopically in all cases. The zinc acetate was in the form of dihydrate except where stated.

TABLE II.
Preparation of zinc tetrabenzporphin from miscellaneous reagents.

Expt. no.	Reagents.	Conditions :		Yield, %.
		Hours.	Temp.	
17	Zn salt of (I) + Zn(OAc) ₂ ·2H ₂ O	4	330°	14
18	Same as 17	1½	390	16
19	(I) + Zn (metal surface specially cleaned)	4	330	4
20	Same as 19	4	350	4
21	Same as 19, but with ZnO and uncleaned metal	4	330	2
22	Same as 19, but with Zn(OAc) ₂ ·2H ₂ O in addition	4	330	4—14*
23	(I) + ZnCl ₂	4	330	2
24	Amide of (I) + Zn	4	325	Nil
25	Amide of (I) + Zn(OAc) ₂ ·2H ₂ O	1½	390	2
26	Methylphthalimidine + Zn(OAc) ₂ ·2H ₂ O	1	390	14

* Variable.

Table II summarises the results obtained on using other reagents. It will be seen that in the reaction with zinc acetate, the zinc salt of carboxymethylphthalimidine (I) was as effective as the free acid (Expts. 17, 18). Expts. 19—23 indicate that zinc acetate was the best form in which to supply the metal. The amide of the acid (I) was comparatively ineffective as an intermediate but the decarboxylated substance, methylphthalimidine, is not far inferior to the acid.

(ii) *Sulphonation of Macrocyclic Pigments.*

(1) *Phthalocyanine.*—A solution of 5 g. of the metal-free compound in 150 c.c. of fuming sulphuric acid (30% SO₃) was heated for 2 hours at 80—85°. The product was cooled and poured into a mixture of saturated aqueous sodium chloride (2 l.) and ice (500 g.). The fine, flocculent, green precipitate was filtered off on cloth and squeezed dry by hand. It was then dissolved in water, the solution filtered, and the green sodium salt reprecipitated by careful addition of saturated aqueous sodium chloride solution. The pigment was filtered off on hard paper and washed first with 100 c.c. of 70% alcohol and then with 90% alcohol until the washings were free from chloride. The product, dried to constant weight at 135°/1 mm., was a green solid with a red reflex (3.0 g.) (Found : S, 12.5; 12.8; Na, 8.0, 7.85. Calc. for $C_{32}H_{15}O_{12}N_8S_4Na_2$: S, 14.3; Na, 7.7%. Calc. for $C_{32}H_{15}O_9N_8S_3Na_2$: S, 11.7; Na, 8.4%. Calc. for $C_{32}H_{15}O_6N_8S_2Na_2$: S, 12.0; Na, 5.8%). The salt is soluble in water, giving an intensely green solution. There are no definite bands in the absorption spectrum, which consists of diffuse absorption in the far red. The salt is strongly hygroscopic.

(2) *Tetrabenztriazaporphin.*—2 g. of the metal-free pigment (Barrett, Linstead, and Tuey, *loc. cit.*) were dissolved in a mixture of 30 c.c. of concentrated and 30 c.c. of fuming sulphuric acid (30% SO₃). A red colour developed at once. After 2 days at room temperature the solution was poured on ice (400 g.) which gave a deep green precipitate. The pigment was dissolved in alkali, and the solution filtered and treated with acid. The reprecipitated material was concentrated in a centrifuge to a thick green jelly which was washed with very dilute hydrochloric acid until free from sulphate. The jelly was evaporated in a desiccator over alkali and the resulting powder was dried at 80°/1 mm.; the yield was 520 mg. (20%). The *tetrabenztriazaporphinsulphonic acid* (mainly mono-) was slightly hygroscopic (Found : S, 6.2, 6.4. $C_{33}H_{19}O_3N_7S$ requires S, 5.4%. $C_{33}H_{19}O_6N_7S_2$, the disulphonic acid, requires S, 9.5%). There were two diffuse bands in the absorption spectrum with maxima at 6550 and 6800 Å.

When a similar experiment was carried out but with 30% oleum and no concentrated sulphuric acid, no green pigment could be recovered after 30 minutes or next morning.

(3) *Zinc Tetrabenzporphin.*—A solution of 50 mg. of the pigment in 20 c.c. of sulphuric acid (30% SO₃) was kept overnight at room temperature. The green solution when poured on ice gave a brown precipitate. This dissolved in aqueous ammonia to a green solution, showing a diffuse absorption band with maximum at 6320 Å.

(4) *Oxidation of Sulphonated Compounds.*—The solution of phthalocyaninesulphonic acid in dilute aqueous sulphuric acid is green. Addition of a drop of N/20-ceric sulphate gives a transitory blue flash which reverts in a second to the original green. This can be repeated until all the pigment has been oxidised and the solution is colourless (see below). Addition of a drop of permanganate solution to the green solution of tetrabenztriazaporphinsulphonic acid in dilute alkali also gives a deep blue which fades slowly (1 min.) to the original green. A similar experiment on zinc tetrabenztriazaporphinsulphonic acid with permanganate gave a persistent deep brown colour.

A sample of about 25 mg. of sodium phthalocyaninesulphonate was weighed accurately into a flask, dissolved in dilute sulphuric acid, and oxidised at room temperature with *N*/20-ceric sulphate solution. The complete oxidation took about 10 minutes; the addition of each drop of reagent produced the transitory blue already referred to. The pigment acted as its own indicator, the final disappearance of colour being effected by the addition of 0.03 c.c. of the reagent. The results are tabulated below :

Weight of pigment, mg.	0.0497 <i>N</i> -Ce(SO ₄) ₂ , c.c.	Atoms of oxygen/mole.
22.4	1.05	0.98
32.0	1.50	0.99

The molecular weight used in this calculation was 846, being derived from the analytical figures already given for the sodium salt, which correspond to 3.34 g.-atoms of sulphur per molecule.

Samples of about 20 mg. each of tetrabenztriazaporphinsulphonic acid were accurately weighed and dissolved in 20 c.c. of warm water. The green solution was treated with 5 c.c. of concentrated sulphuric acid, which gave a green suspension. Samples were treated with 10 c.c. of *N*/20-ceric sulphate solution under the various conditions indicated in the table below, and the product in each case was cooled, treated with 10 c.c. of *N*/20-ferrous sulphate solution, and back-titrated with ceric sulphate. The addition of ceric sulphate to the original suspension at room temperature gave a deep blue colour, stable for several minutes.

Oxidation of tetrabenztriazaporphinsulphonic acid by ceric sulphate.

Conditions :		Uptake of oxygen (g.-atoms/mol.) :		Conditions :		Uptake of oxygen (g.-atoms/mol.) :	
Time, mins.	Temp.	Obs.	Corr.*	Time, mins.	Temp.	Obs.	Corr.*
2	0°	1.1	1.1	60	100°	4.2	4.0
9	25	1.3	1.3	60	100	4.2	4.0
				60	100	4.4	4.1

* The correction used is based on the observed oxidation of phthalimide under the same experimental conditions (see following paper). The assumption is made that 4-sulphophthalimide behaves similarly.

(5) *Fission Products of Phthalocyaninesulphonic Acid: Orientation of Sulphonation.*—Sodium phthalocyaninesulphonate (1.64 g.) was dissolved in 60 c.c. of warm water. The solution was acidified with 4 c.c. of acetic acid and titrated with 80 c.c. of *M*/100-permanganate solution. The light brown solution was reduced to a faint green colour with a little sodium hydrogen sulphite and was then continuously extracted with ether. The extract yielded 0.14 g. of phthalimide, *m. p.* and mixed *m. p.* 229—231° (this corresponds to the sulphonic acid possessing an average of 0.5 unsulphonated benzene ring per molecule, whereas the analytical figures correspond to an average of 0.66 unsulphonated unit. The yield of phthalimide is therefore 75%). The aqueous solution after the ether-extraction was evaporated to 50 c.c., freed from manganese with aqueous ammonia and ammonium sulphide, treated with 3 c.c. of 10% aqueous sodium hydroxide, and evaporated further to 10 c.c. This solution was transferred to a Carius tube, evaporated to 2 c.c., and treated with 3 g. of solid sodium hydroxide. The tube was sealed and heated to 170—180° for 5 hours. [Under these conditions Dimroth and Fick (*Annalen*, 1916, **411**, 323) have shown that 4-sulphophthalic acid yields 4-hydroxyphthalic acid.] The contents were taken up in 100 c.c. of hot water, and the solution acidified and extracted continuously with ether. The extract yielded crude 4-hydroxyphthalic acid as a white powder (430 mg.). This was esterified with diazomethane, and the phenolic ester extracted with aqueous alkali. Acidification of the alkaline extraction followed by basification with sodium carbonate and extraction with ether yielded dimethyl 4-hydroxyphthalate (260 mg., 20%), *m. p.* 102—103°. After 3 crystallisations from toluene the *m. p.* became constant at 104.2—104.7°. This *m. p.* is given in the literature as 107—108° (Bentley and Weizman, *J.*, 1907, **91**, 100) and 102° (Graebe and Réé, *J.*, 1886, **49**, 524).

Authentic material was prepared for reference by the following route. 4-Aminophthalimide was prepared and converted into 4-hydroxyphthalimide following Levy and Stephen (*J.*, 1931, 79). The hydroxy-imide was not, however, isolated; instead, the solution obtained from the diazotisation of the amino-imide (5 g.) was boiled for 3 hours. It was then saturated with salt and extracted with ether. Removal of the ether left a crystalline solid which was esterified with methanolic sulphuric acid (50 c.c. methanol, 40 c.c. sulphuric acid; 2 hours at 65°). Dimethyl 4-hydroxyphthalate was isolated from the reaction product by means of ether and purified as described above; the yield was 1.8 g. (30%) and the *m. p.* 105.2—105.5°, not depressed by the material prepared from phthalocyaninesulphonic acid.

(6) *Miscellaneous Experiments with Sulphonated Compounds.*—(a) Sodium phthalocyaninesulphonate (100 mg.) was fused with 2 g. of potassium hydroxide at 250° for 1 minute under nitrogen. The melt when cooled and acidified gave a very pale green solution but no precipitate.

(b) The same sodium salt (1 g.) was heated in a Carius tube with 2 g. of sodium hydroxide and 1 c.c. of water, following Dimroth and Fick (*loc. cit.*). After 5 hours at 220—250°, the solution was cooled and dissolved in water. A slight green colour remained. Acidification yielded no precipitate, and ether-extraction left the green colour in the aqueous layer: it is presumably due to a little unchanged phthalocyaninesulphonate or perhaps to a partly hydroxylated pigment. Extraction of the acidified solution with ether and removal of the solvent left *m*-hydroxybenzoic acid as a colourless solid. Esterification of this with methanolic sulphuric acid gave methyl *m*-hydroxybenzoate, *m. p.* and mixed *m. p.* 71—73°.

(c) Following Limpricht's general procedure (*Ber.*, 1877, **10**, 315), 100 mg. of sodium phthalocyaninesulphonate were heated for 5 hours at 295° in a Carius tube with 2 c.c. of concentrated hydrochloric acid

but the product was colourless. Further, it was not possible to regenerate phthalocyanine from the sulphate by refluxing it with 70% or 30% sulphuric acid. Introduction of mercury or its salts (Lauer, *J. pr. Chem.*, 1931, **130**, 194; 1932, **135**, 182; 1933, **138**, 81) failed to catalyse the elimination of sulphonic groups and led to decomposition as before.

(iii) *Halogenation of Zinc Tetrabenzporphin.*

(1) *Addition under Mild Conditions* (see Barrett, Bradbrook, Dent, and Linstead, *loc. cit.*, p. 1824).—A known weight (about 0.5 g.) of powdered zinc tetrabenzporphin was shaken in a tall glass-stoppered cylinder with a dilute solution of bromine in carbon tetrachloride of known normality. The solid was allowed to settle, and the amount of bromine left unchanged was determined by titration of an aliquot portion of the solution with sodium thiosulphate solution. Results are given below.

Addition of bromine to zinc tetrabenzporphin.

Expt.	Time of reaction, hrs.	Bromine absorbed, g.-atoms/mole.	Expt.	Time of reaction, hrs.	Bromine absorbed, g.-atoms/mole.	
	Bromine soln. = 0.1N.			Bromine soln. = 0.5N.		
1	2.5	4.9	4	0.5	6.9	
2	4	5.7	5	1.5	7.1	
3	44	6.2	6	17	7.1	

The products of Expts. 3 and 6 were heated with 100 c.c. of N-sodium hydroxide in 50% ethanol at 90° for 2 hours. The pigments were recovered and the bromine determined (Found: 0.8, 0.8 g.-atom of bromine per mole). This shows that the bulk of the 6–7 g.-atoms of bromine taken up under the above conditions is in the form of an unstable addition compound.

(2) *Substitution.*—(a) 200 Mg. of zinc tetrabenzporphin, in a Carius tube from which the air had been displaced with nitrogen, were treated with 1.6 c.c. of bromine which had been dried as vapour over calcium sulphate and condensed in an air-free vacuum system. One drop of phosphorus tribromide was added, the tube sealed and heated at 250° for 4 hours, and the excess of bromine then removed with aqueous sodium hydrogen sulphite. The residue of brominated pigment was ground with 5% aqueous sodium hydroxide which left 670 mg. of a black solid (Found: Br, 71.5. Calc. for $C_{36}H_8N_4Br_1Zn$: Br, 71.0%). Extraction of the solid with solvents showed that it was not homogeneous; *e.g.*, when 240 mg. were extracted with ether, 160 mg. remained as an insoluble residue containing slightly less bromine (Found: Br, 68.2. Calc. for $C_{36}H_8N_4Br_{1.5}Zn$: Br, 68.3%).

(b) 100 Mg. of powdered zinc tetrabenzporphin were refluxed for 24 hours with thionyl chloride and sulphuryl chloride (10 c.c. of each). The reagents were removed under reduced pressure, leaving a brown tarry solid, which was shaken with water containing a trace of iodine, and then ground with dilute sodium hydroxide. This left 150 mg. of a greenish solid giving a yellow-brown solution in pyridine (Found: Cl, 40.5. $C_{36}H_8N_4Cl_{1.1}Zn$ requires Cl, 41.0%). Under the conditions which convert phthalocyanine into a highly chlorinated derivative (action of chlorine gas on a solution in phthalic anhydride in the presence of antimony pentachloride at 250°) zinc tetrabenzporphin was completely decomposed. Another distinction between the two classes of macrocyclic pigment is that the action of bromine in boiling nitrobenzene decomposes zinc tetrabenzporphin but gives a good yield of brominated phthalocyanine.

Halogen and sulphur analyses were carried out by the methods of caustic-alkali fusion described by Treadwell and Hall ("Analytical Chemistry," II, 8th edn., 1935, pp. 307, 337). These methods gave satisfactory analytical figures for known bromine- and sulphur-containing phthalocyanines.

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