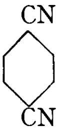
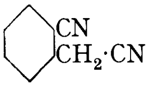
217. *Phthalocyanines. Part VI. The Structure of the Phthalocyanines.*

By C. E. Dent, R. P. Linstead, and A. R. Lowe.

Comparative experiments have shown that the reagents which readily yield phthalocyanines with *o*-phthalonitrile give no similar products with terephthalonitrile (I), homophthalonitrile (II), *o*-xylylene dicyanide (III), *o*-cyanocinnamonitrile (IV), and 2 : 2′-diphenonitrile (V).

(I.)





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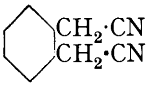
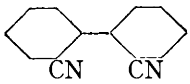


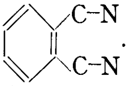
(III.)

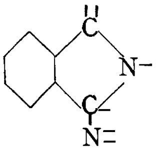
(IV.)

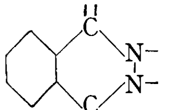


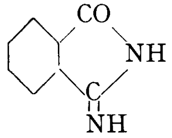
(V.)

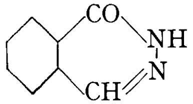
These facts indicate that the two nitrile groups participating in phthalocyanine formation must be linked to adjacent carbon atoms of an aromatic nucleus and cannot be separated by an additional saturated atom or by an extended unsaturated or aromatic unit. The obvious inference, that the production of a phthalocyanine involves the formation of a ring fused to the aromatic nucleus in the 1 : 2 positions and containing six atoms or less, is supported by the hydrolysis and oxidation of phthalocyanines to derivatives of *o*-phthalic acid.

The evidence of synthesis and of fission and the results of analysis * both indicate the presence of the skeleton . The analytical figures prove that the non-benzenoid carbon and the nitrogen atom carry no oxygen and little or no hydrogen (the exact content of hydrogen, which is left uncertain by the figures, is discussed later). The only structural units which satisfy these conditions are an *iso*indole ring with an extracyclic nitrogen atom (VI) and a phthalazine ring (VII) :

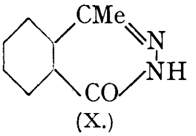

(VI.)

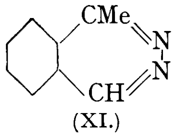

(VII.)

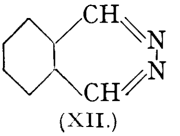

(VIII.)


(IX.)

The available evidence is strongly in favour of the first of these formulæ. The controlled decomposition of phthalocyanine to phthalimide and ammonium nitrate by nitric acid (p. 1021) indicates that the molecule contains two dissimilar types of nitrogen atom. This is not, however, a definite proof, because it is known that certain phthalazines can be converted into derivatives of *iso*indole by extrusion of one nitrogen atom, as, for example, in the reduction of chlorophthalazines to dihydro*iso*indoles (Gabriel and Neumann, *Ber.*, 1893, **26**, 521, 705). A comparison has therefore been made of the capacity of the two systems for phthalocyanine formation. Experiments with iminophthalimidine (VIII) and the isomeric phthalazone (IX) have shown that the *iso*indole derivative readily yields phthalocyanines under conditions where phthalazone is unchanged. Indeed we have been unable to obtain definite indications of phthalocyanine formation by prolonged treatment of (IX) under the most favourable conditions. Further experiments by Dr. E. G. Noble and one of us show that methylphthalazone, methylphthalazine, and phthalazine itself (X, XI, and XII) also give negative results, the last even in the presence of oxidising agents such as cupric and ferric chlorides.


(X.)


(XI.)


(XII.)

The *iso*indole formula is also to be preferred on stereochemical grounds. Inspection of the complete formulæ (such as XIV) given below, which contain four C_8 units, shows that it would be impossible to join four phthalazine nuclei in the form of a suitable large complex

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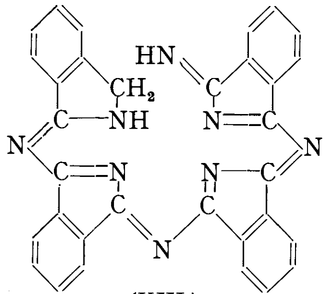
* It will be convenient to summarise here the analytical data for pure phthalocyanine from various sources :

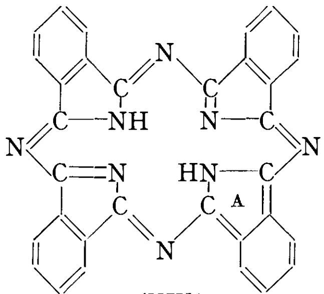
	Method of preparation.	C, %.	H, %.	N, %.
Found	Mg compound (*ex* cyanobenzamide) + H_2SO_4	74·8	3·6	21·5
	,, ,, + HCl	74·0	3·7	—
	,, (*ex* phthalonitrile) + H_2SO_4	74·6	3·6	—
	Cyanobenzamide + antimony	74·3	3·7	21·6
	Phthalonitrile + sodium amyloxide	74·5	3·8	21·5
Calc.	for $(C_8H_4N_2)_4$	75·0	3·1	21·9
	for $(C_8H_4N_2)_4H_2$	74·7	3·5	21·8
	for $(C_8H_4N_2)_4H_4$	74·4	3·9	21·7

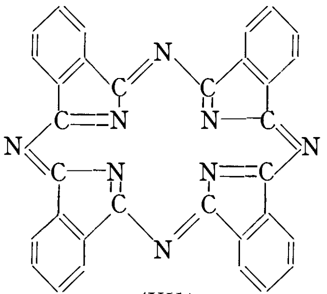
ring, as the components would have to be linked directly without the intervention of the connecting atoms, which in the *iso*indole formula provide the necessary angular divergence.

The intense colour of the phthalocyanines makes it obvious that their molecules cannot be composed of one *iso*indole ring. The analyses of the metallic derivatives show that four such units are combined for every atom of metal—an aggregation which is confirmed by the molecular weight of magnesium phthalocyanine (see Part V). The close similarity in physical properties of free phthalocyanine and its metallic derivatives indicates that the parent compound also has four C_8 units in the molecule. A four-unit formula is further supported by the results of the quantitative oxidation of both the free and the metallic phthalocyanines.

The only reasonable way in which these *iso*indole units can be joined is by means of the extracyclic nitrogen atoms : the remaining valencies will then form a conjugated chain, in keeping with the strong colour. This leads to the " chain " formula (XIII) or the ring formula (XIV).


(XIII.)

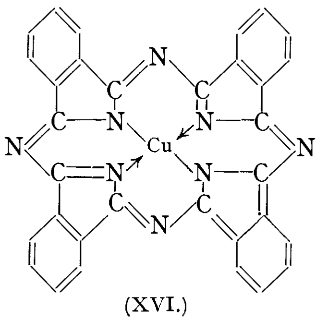

(XIV.)

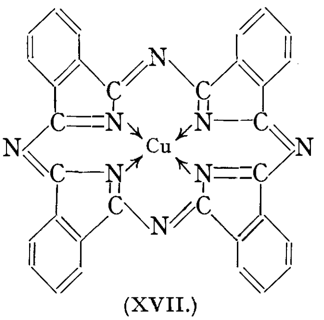

(XV.)

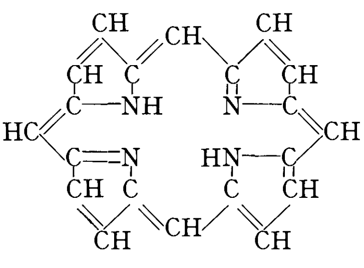
If two imino-hydrogen atoms are left available for the fixation of the metal, (XIII) is equivalent to $(C_8H_5N_2)_4$ and (XIV) to $(C_8H_4N_2)_4H_2$. The analytical difference is too small to be detectable. The formation of copper phthalocyanine, $(C_8H_4N_2)_4Cu$, from phthalonitrile, and copper can only be simply accounted for on the basis of the ring formula, and the chain formula is excluded by the results of quantitative oxidation (p. 1038).

A slightly different ring formula is (XV), which contains no imino-hydrogen atoms and has all the aromatic rings in the benzenoid condition, whereas in (XIV) one ring is *o*-quinonoid.

Formulæ (XIV) and (XV) differ in their implications respecting the attachment of the metal on the derivatives. Copper phthalocyanine could be expressed as a derivative of (XIV) by the formula (XVI), in which the metal has displaced two hydrogen atoms and is attached by covalencies to two *iso*indole nitrogen atoms (and may be co-ordinated to the other two ; see p. 1037). In a formula based on (XV), however, the metal would be held purely by co-ordinate links to the nitrogen atoms (XVII).


(XVI.)


(XVII.)


(XVIII.)

These formulæ are analogous to the alternative representations of the complex metallic derivatives of indigo (Kunz and co-workers, *Ber.*, 1922, **55**, 3699 ; 1923, **56**, 2027 ; 1925,

58, 1860; 1927, **60**, 367; 1930, **63**, 2600) for which the formula involving "primary" valencies (corresponding to XVI) has been proved correct by Kuhn and Machemer (*Ber.*, 1928, **61**, 118).

There is experimental evidence in favour of formulæ (XIV) and (XVI) and opposed to (XV) and (XVII). The stability of the copper compound in the vapour phase at 580° would be inconceivable if the metal were held solely by co-ordinate links. If there were no imino-hydrogen atoms in phthalocyanine, hydrogen should be liberated during the preparation of this substance by the action of sulphuric acid on the magnesium compound : none has been observed. If, on the other hand, the imino-hydrogen atoms are present, the formation of the metallic compounds from free phthalocyanine should be accompanied by an evolution of hydrogen. We find, however, that hydrogen is slowly evolved when magnesium alone is boiled with quinoline; the reaction, therefore, is not diagnostic.

It was hoped to obtained decisive evidence by the Tschugaeff–Zerewitinoff method for the estimation of active hydrogen (*Ber.*, 1902, **35**, 3912; 1907, **40**, 2023, etc.; compare Hibbert and Sudborough, J., 1904, **85**, 933, etc.), which has recently been applied to the investigation of complex metallic compounds and their precursors by Kuhn and others (*loc. cit.*; *Ber.*, 1928, **61**, 128), although it has not been so successful in the porphyrin, hæmin, and chlorophyll series (see a summary by Fischer and Rothemund, *Ber.*, 1931, **64**, 201). Unfortunately the method or known modifications could not be applied to the phthalocyanines owing to their insolubility in the usual media, and the use of quinoline was also unsatisfactory (p. 1038).

Fission by oxidation provided the desired evidence. It was known that phthalocyanine and its heavy-metal derivatives were stable in cold sulphuric acid solution for long periods, but were decomposed by hot acid permanganate so readily that suspensions in dilute sulphuric acid could be titrated with this reagent. The fission of a molecule of a phthalocyanine of formula (XIV) to phthalimide requires one atom of oxygen (*a*), whereas a molecule of formula (XV) requires no oxygen (*b*) :

$$(a)\ (C_8H_4N_2)_4H_2 + 7H_2O + O = 4C_8H_5O_2N + 4NH_3$$
$$(b)\ (C_8H_4N_2)_4 + 8H_2O = 4C_8H_5O_2N + 4NH_3$$

The ease of the oxidative fission is therefore strong evidence in favour of (XIV), and to make this conclusive, we endeavoured to find conditions under which equation (*a*) could be realised quantitatively. This could not be achieved by the use of permanganate, as there was some autocatalytic decomposition of the reagent, oxygen being partly liberated and partly dissolved in the solution. Ceric sulphate, which has been used as a stable substitute for permanganate in inorganic analyses (Mitchell and Ward, "Modern Methods in Quantitative Chemical Analysis," p. 15), proved to be excellent for our purpose. We are indebted to Dr. A. M. Ward for suggesting its use.

Ceric sulphate reacts very rapidly with a suspension of phthalocyanine in dilute sulphuric acid at room temperature. Exactly one atom of oxygen is taken up (for each four C_8 units) and about 90% of the theoretical quantity of phthalimide can be isolated from the product. Under similar conditions copper phthalocyanine is oxidised according to the equation :

$$(C_8H_4N_2)_4Cu + 8H_2O + O = 4C_8H_5O_2N + CuO + 4NH_3$$

Oxidation of magnesium phthalocyanine (dihydrate) proceeds similarly :

$$(C_8H_4N_2)_4Mg,2H_2O + 6H_2O + O = 4C_8H_5O_2N + MgO + 4NH_3$$

This shows that the combined oxygen in this compound is not effective for oxidation.

Phthalonitrile takes up no oxygen under these conditions, which justifies experimentally the contention that the hydrolysis of a substance of formula (XV), which is a polymeride of phthalonitrile, to phthalimide would not involve oxidation (equation *b*).

The absence of oxidisable hydrogen in the metallic derivatives and its presence in the parent compound proves that a bivalent metal takes the place of two atoms of hydrogen and is therefore bound by covalencies.

If phthalocyanine had the " open-chain " structure [XIII = $(C_8H_5N_2)_4$], each molecule should either take up two atoms of oxygen and form four molecules of phthalimide or take up one atom of oxygen and form three molecules of phthalimide and one molecule of phthalimidine. Both of these possibilities, and hence the open-chain structure, are therefore excluded and the structures represented by (XIV) and (XVI) are proposed for phthalocyanine and its metallic derivatives. The *fine* structure, *i.e.*, the relative positions of the imino-hydrogen atoms and the consequent arrangement of the double bonds, cannot be decided by the chemical evidence. The hydrogen atoms have been placed on opposite instead of on adjacent rings in the formulæ on the basis of *X*-ray measurements by Dr. J. M. Robertson.

The stability of copper phthalocyanine indicates that the metal is co-ordinated, presumably with the other two *iso*indole nitrogen atoms, but it is necessary to consider this more fully in relation to the stereochemistry of the molecule as a whole. On the basis of formula (XIV) the cyclic framework of phthalocyanine should exist in one plane and the only possibility of deviation lies in the ability of ring A to rotate on the two single links connecting it with the extracyclic nitrogen atoms. If all the rings lie in one plane, the valencies connecting the imino-nitrogen atoms will be inclined to this, so that the hydrogen atoms of phthalocyanine will lie out of the great plane.

Both *cis*- and *trans*-forms of this compound then become possible, according to the relative position of the two hydrogen atoms. Models show that a metal exhibiting normal tetrahedral symmetry can take the place of the two hydrogen atoms without appreciable strain in a *cis*-phthalocyanine and with but little strain in a *trans*-form. On the other hand, if the other two *iso*indole nitrogen atoms become co-ordinated, the new links would tend to lie in the great plane. Hence, for a metal with tetrahedral symmetry to be co-ordinated, the molecule must accommodate (1) some distortion of the nitrogen valencies and (2) considerable distortion of the metallic valencies. A metal with planar symmetry (*e.g.*, nickel) could, however, be co-ordinated in the centre of the molecule with distortion of only two nitrogen valencies. It therefore appears that, if co-ordination of a metal normally exhibiting tetrahedral symmetry occurs, either the molecule must lose its planar configuration or the normal direction of the metallic valencies must be modified.

Connexion with the Porphyrins.—There is a close connexion between phthalocyanines of formulæ (XIV) and (XVI) and the porphyrins, which form the basis of many important natural colouring matters and have been shown by Küster, Willstätter, Hans Fischer, and others to contain the fundamental porphin ring (XVIII). (The imino-hydrogen atoms are placed on opposite rings by analogy with those of phthalocyanine.) This differs from phthalocyanine in two respects; the pyrrole units do not carry benzene nuclei and are connected to one another by methine groups in place of nitrogen atoms. These factors would not be expected to influence the general spatial arrangement or the stability of the complex molecule, for it is well known that a nitrogen atom may take the place of a methine group in rings without greatly affecting their general character. In agreement with this, there are a number of resemblances between the two types : both are stable to alkalis, less so to acids; both are highly coloured, and form complex metallic compounds; and both can be degraded by oxidation to the imides of dibasic acids. Moreover, there is a similarity in the order of stability of the metallic derivatives of the porphyrin and of the phthalocyanine series. For instance, the metallic phthalocyanines may be compared with the corresponding derivatives of substances of the type of phytochlorin and phytorhodin. Willstätter and Stoll (" Chlorophyll," 1913, Chapter XIX) state that the magnesium compounds of these are intermediate in stability between the potassium derivatives, which lose the metal in dilute alcoholic solution, and the copper compounds, which are of " unparalleled stability." * The spatial arrangement of the great ring and the metal may be presumed to be identical in the phthalocyanines and the porphyrins and it is hoped that further investigation of the metallic phthalocyanines may throw some light on the general stereochemical problem.

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* Geh. Professor Dr. R. Willstätter predicted the great stability of copper phthalocyanine to one of us (R. P. L.) some months before the compound was first isolated.

EXPERIMENTAL.

Experiments with Dinitriles other than o-*Phthalonitrile.*—Terephthalonitrile, homophthalonitrile, *o*-xylylene dicyanide, *o*-cyanocinnamonitrile, and 2 : 2′-diphenonitrile were each treated with the following reagents: magnesium, copper, and cuprous chloride at the boiling point of the dinitrile, and with sodium amyloxide in boiling amyl alcohol. No coloured products could be isolated in any of the experiments. *o*-Xylylene dicyanide and *o*-cyanocinnamonitrile gave a green colour with sodium amyloxide, but no pigment could be isolated from the solutions. 2 : 2′-Diphenonitrile gave a similar green colour with molten metallic sodium.

Comparison of Iminophthalimidine and Phthalazone (VIII *and* IX).—As *o*-cyanobenzamide passes apparently completely into iminophthalimidine above its melting point (Braun and Tcherniac, *loc. cit.*), the results of Part II serve for one side of this comparison. Pure recrystallised iminophthalimidine (m. p. 203°), made by acidification of a solution of *o*-cyanobenzamide in alkali with acetic acid at 0°, also readily gave magnesium phthalocyanine when heated with magnesium oxide at 240—260°. Phthalazone, m. p. 182°, made from phthalide by Gabriel and Neumann's method (*Ber.*, 1893, **26**, 521), yielded no trace of green or blue colour when heated even to the boiling point (337°) with sodium, sodium amyloxide, magnesium, or cuprous chloride. With magnesium oxide a weak green colour was formed, but no pigment could be isolated from the product. Zinc chloride also gave a slight green colour.

Attempted Determinations of "Active" Hydrogen.—A two-chambered reaction vessel similar to that recommended by Zerewitinoff (*Ber.*, 1907, **40**, 2023) was used. The Grignard compound was prepared from methyl iodide and magnesium in pure amyl ether. The quinoline was freed from aromatic bases by the action of nitrous acid and converted into the dichromate, which was repeatedly crystallised. The base was regenerated with alkali and distilled in steam and under reduced pressure, b. p. 115°/16 mm. It gave no colour with acid hypochlorite and no methane with the Grignard reagent.

The procedure followed that previously used (*loc. cit.*; Sudborough and Hibbert, J., 1904, **85**, 933; 1909, **95**, 477) except that quinoline was employed as solvent. The results were satisfactory for phthalimide (Found: active H, 1·0, 0·9, 1·0, 0·9, 1·1, 1·0 atom per molecule). Phthalocyanine slowly evolved methane with the reagent, but the results of a large number of experiments varied with the time of reaction to such an extent that they could not be satisfactorily corrected by blank experiments.

Quantitative Oxidations.—The following results were obtained by dissolution of the phthalocyanine in concentrated sulphuric acid, precipitation with water, and titration at the boiling point with *N*/20-potassium permanganate: Found for phthalocyanine: oxidisable H, 0·49, 0·56. $(C_8H_4N_2)_4H_2$ requires 0·39%. Found for copper phthalocyanine: oxidisable Cu, 15·7, 15·7. $(C_8H_4N_2)_4Cu$ requires 11·05%. The results for both compounds are high in the same proportion and the method must therefore be at fault. When the precipitated copper phthalocyanine was filtered off, washed, and titrated in dilute sulphuric acid, a rather better result was obtained (Cu, 12·9%).

Use of ceric sulphate. A known weight (about 0·3 g.) of the finely divided compound was triturated with a little dilute sulphuric acid, and a known excess of exactly *N*/10-ceric sulphate solution (Mitchell and Ward, *op. cit.*) added. The bulk of the pigment rapidly disappeared. To ensure the completion of the reaction, the solution was kept at 60° until clear, any lumps being crushed. *N*/10-Ferrous ammonium sulphate equivalent to the original amount of ceric sulphate was then added, and the excess of ferrous salt titrated with *N*/10-ceric sulphate, xylene cyanole FF being used as indicator. The colour changes from greenish-yellow to brown in the presence of excess of the ceric salt; the end-point is sharp and can be approached from either side. The final ceric sulphate titre is equivalent to the amount originally employed to oxidise the phthalocyanine.

The results are summarised below. The last column gives the molecular weight assumed in the calculations:

	Found.	Calc.	M.W.
% Oxidisable H in phthalocyanine	0·39, 0·38	0·39	514
,, Mg in magnesium phthalocyanine (dihydrate)	4·3, 4·2	4·25	572
,, Cu in copper phthalocyanine	11·2, 10·6	11·05	576

When the solution obtained in the oxidation of the magnesium compound was kept for 2 days, long needles of phthalimide formed (yield, 87·5%), m. p. and mixed m. p. 228°. The mother-liquor on continuous extraction with ether for a further 5 days yielded a further 4·5% of phthalimide. Similarly, phthalocyanine itself yielded 89% of pure phthalimide.

Our thanks are due to Professor J. F. Thorpe, C.B.E., F.R.S., for his kindness in enabling us to carry out this work and for his encouragement and advice. We are also indebted to Imperial Chemical Industries Limited for grants and gifts of chemicals, to Dr. E. H. Rodd for many valuable suggestions, to Dr. H. F. Harwood for advice on analytical matters, and to the Salters' Company for a grant to one of us (A. R. L.).

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