385. *Phthalocyanines. Part VIII.* 1 : 2-*Naphthalocyanines.*

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THE ten dicyanonaphthalenes (preceding paper) have been tested for their ability to form compounds of the phthalocyanine series. The tests (p. 1746) include treatment with various metals, metallic oxides and chlorides. 1 : 2- and 2 : 3-Dicyanonaphthalene combine readily with a number of metallic reagents to yield green colouring matters; the other isomerides show no reaction whatever. The green compounds derived from 1 : 2-dicyanonaphthalene are of the phthalocyanine type and the behaviour of its isomerides thus verifies the statement that "the two nitrile groups participating in phthalocyanine formation must be linked to adjacent carbon atoms of an aromatic nucleus" (Dent, Linstead, and Lowe, J., 1934, 1034). It is of particular interest that 1 : 8-dicyanonaphthalene yields no such compounds, although the corresponding acid resembles phthalic acid in many respects. It is, however, impossible for this dinitrile to yield a compound of the type of phthalocyanine, on the basis of the formula proposed for the latter (*loc. cit.*).

Owing to the comparative inaccessibility of 2 : 3-dicyanonaphthalene we have confined our attention to the 1 : 2-isomeride. The parent acid being regarded as 1 : 2-naphthalic acid, the derived pigments are conveniently named 1 : 2-naphthalocyanines, more strictly tetra-3 : 4-benzphthalocyanines (see I). Preliminary experiments with a number of metals showed that the *copper, magnesium, zinc,* and *lead* derivatives were very easily formed.* Copper and zinc react with 1 : 2-dicyanonaphthalene at 270—300°, *i.e.*, a rather higher temperature than that necessary for the corresponding reaction with phthalonitrile. The reaction is exothermic, but less so than in the simpler series. Magnesium reacts only at the boiling point of the nitrile (370°). The lead derivative is prepared from litharge and the dinitrile, like the corresponding phthalocyanine. The products are obtained in good yields as rather dark green masses with a purple to blue lustre; there is no appreciable side reaction.

The metallic naphthalocyanines show little tendency to sublime, probably on account of their very large molecular weight, but can be purified by crystallisation from suitable high-boiling solvents. They are rather more soluble than the phthalocyanines, but, unlike the latter, do not crystallise well. Magnesium 1 : 2-naphthalocyanine is exceptional;

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* Our thanks are due to Dr. A. R. Lowe for carrying out a number of preliminary experiments in both the 1 : 2- and the 2 : 3-series.

two isomeric forms have been isolated, one of which (α-form) is freely soluble in cold ether and has been obtained macrocrystalline.

Analysis of the purified metallic compounds shows them to have the general formula $(C_{12}H_6N_2)_4M$, where M is a bivalent metal. The compounds are therefore simply related to the known metallic phthalocyanines $(C_8H_4N_2)_4M$, in agreement with the close resemblance between their physical and chemical properties.

The stability of the metals towards concentrated sulphuric acid is also analogous. Zinc and copper naphthalocyanines give purple solutions which regenerate the unchanged compounds on dilution. On the other hand the lead and α-magnesium compounds are decomposed, the metal is eliminated, and free 1 : 2-*naphthalocyanine*, $(C_{12}H_6N_2)_4H_2$, is formed. When this is boiled with metals in chloronaphthalene, it regenerates the metallic derivatives.

The 1 : 2-naphthalocyanines show an even greater general stability to heat and reagents than the phthalocyanines. In particular they are only slowly oxidised by nitric acid or ceric sulphate. On this account it has not been possible to prove the presence of two oxidisable hydrogen atoms in free naphthalocyanine by quantitative oxidation (Dent, Linstead, and Lowe, *loc. cit.*). α-Magnesium naphthalocyanine, however, is more readily attacked and the oxygen uptake from cold acid ceric sulphate agrees approximately with that required for the equation

$$(C_{12}H_6N_2)_4Mg + 8H_2O + O = 4C_{12}H_7O_2N + 4NH_3 + MgO$$

1 : 2-Naphthalimide and ammonium sulphate are formed. This proves that the metal is combined in the same manner in the 1 : 2-naphthalocyanines as in the phthalocyanines.

The parallelism between the two series also appears in the reaction between cupric chloride and 1 : 2-dicyanonaphthalene (cf. Dent and Linstead, J., 1934, 1027). These react exothermically at 260° with the formation of hydrogen chloride and *copper chloro-1 : 2-naphthalocyanine* :

$$CuCl_2 + 4C_{12}H_6N_2 = (C_{12}H_6N_2)_3Cu(C_{12}H_5ClN_2) + HCl$$

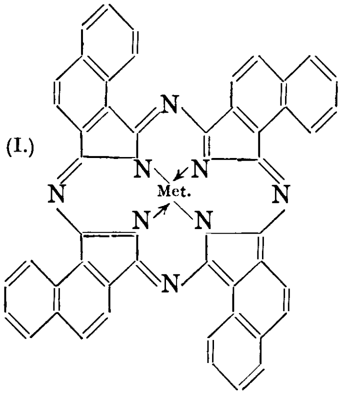
When the product was decomposed with concentrated nitric and sulphuric acids, all the chlorine appeared in the organic fission product and no chloride ion was formed. This shows that the chlorine is nuclear, but its position is unknown.

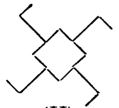
The most interesting feature of the series lies in the existence of isomerides, which was first noticed in the case of the magnesium compound. The crude product of the interaction of magnesium and 1 : 2-dicyanonaphthalene is a mixture of a bright green, ether-soluble α-form and a dark green, insoluble β-form in the ratio 2·5 : 1. The α-form does not form a hydrate, although the unusual solubility in ether, acetone and ethyl acetate indicates a tendency to solvation. The β-form is normally isolated as the *monohydrate*, which loses its water at 215°. The anhydrous form readily regains one molecule of water, but there is no tendency for the formation of a dihydrate as with magnesium phthalocyanine. Like the α-isomeride, the β-magnesium compound yields 1 : 2-naphthalimide on oxidation with ceric sulphate. The two magnesium compounds yield *two different metal-free compounds* on treatment with sulphuric acid. When these are heated with magnesium, they regenerate the isomeric α- and β-magnesium derivatives severally : hence there is a persistent structural difference between the two series.

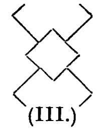
The β-form of free naphthalocyanine is rather darker than the ordinary α-form, but does not show any marked difference in solubility. The free naphthalocyanine prepared from lead naphthalocyanine appears to be identical with the α-isomeride. Moreover, treatment of the α-magnesium derivative with either copper or zinc in boiling chloronaphthalene leads by an exchange of metal to the formation of copper and zinc naphthalocyanines, indistinguishable from those prepared directly from 1 : 2-dicyanonaphthalene. It appears that either the other metallic derivatives all belong to the α-series or their α- and β-modifications are not clearly distinguishable. Slight variations in solubility were indeed noticed, but insufficient for separation.

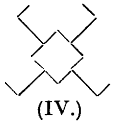
For the interpretation of this isomerism we may take as proved the structural analogy between 1 : 2-naphthalocyanines and phthalocyanines. Four formulæ for the metal-free or metallic derivatives then become possible, one of which is shown in full:

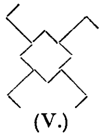
(I.)




(II).


(III.)


(IV.)


(V.)

If we represent the large ring as a lozenge and the aromatic rings by straight lines, this formula may be conveniently symbolised by (II) and the three other possible isomerides by (III), (IV), and (V). The isomerism thus depends upon the relative positions of the four outer benzene rings. We tentatively assign the most symmetrical "swastika" formula (I and II) to the common α-series. The β-series may correspond to one of (III), (IV), and (V) or to a mixture of all three.

It is instructive to compare the easily crystallisable phthalocyanines, which cannot exhibit this isomerism, with the naphthalocyanines, which may be isomeric mixtures and cannot be obtained crystalline except in one case (α-magnesium) where the separation of the mixture is especially easy.

EXPERIMENTAL.

Tests on Dicyanonaphthalenes.—For conversion into substances of the phthalocyanine type, the dinitrile was heated with sodium, sodium ethoxide, sodium amyloxide, magnesium, magnesium oxide, copper-bronze, cuprous chloride, anhydrous cupric chloride, anhydrous zinc chloride, and anhydrous ferric chloride. The 1 : 2- and the 2 : 3-dinitrile gave positive results (green colour, violet reflex) with all these reagents.

General Notes on the Analysis of 1 : 2-*Naphthalocyanines.*—In carbon and hydrogen analyses the burning was complete in 15—20 minutes. Nitrogen estimations were made by the Kjeldahl method, the Dumas method being unsatisfactory owing to the stability of the compounds in the inert atmosphere. Chlorine was determined by Liebig's method. Zinc and magnesium were estimated by ignition to the oxides. Copper in copper chloronaphthalocyanine was determined by oxidation of about 0·2 g. with 20 c.c. of concentrated sulphuric acid and a few drops of nitric acid, concentration to 2 c.c., and dissolution in water. The solution was then neutralised with ammonia, barely acidified with hydrochloric acid, and filtered. The filtrate was reduced with sulphur dioxide, and warmed for 1 hour with an excess of ammonium thiocyanate. After standing overnight, the cuprous thiocyanate was weighed in the usual way. Lead was estimated by boiling the pigment (0·4 g.) with concentrated nitric acid until it was destroyed (2 days). The colourless solution was diluted to 200 c.c., boiled, cooled, and filtered. The filtrate and washings were neutralised with ammonia, made slightly acid with nitric acid, and diluted to 600 c.c. The lead was precipitated as chromate and weighed in the usual manner. Micro-analyses by Schoeller are asterisked.

Copper (with A. R. LOWE; compare also B.P. 410,814).—5 G. of 1 : 2-dicyanonaphthalene were heated with 1 g. of reduced copper for 1 hour at 250—260° by means of a mixed nitrate bath. From the cold powdered melt, boiling alcohol extracted 1·75 g. of unreacted dinitrile. The residue was dissolved in cold concentrated sulphuric acid, and the dark purple solution poured on ice. The green precipitate was filtered off, and washed with hot water (until free from acid), alcohol and ether. Yield, 46%. Two crystallisations from quinoline yielded pure *copper* 1 : 2 *naphthalocyanine* as a green mass with a violet reflex (Found: C, 74·0; H, 3·7; N, 14·3; Cu, 8·0. $C_{48}H_{24}N_8Cu$ requires C, 74·3; H, 3·1; N, 14·4; Cu, 8·2%). The pure compound dissolved in sulphuric acid to give a blue solution, from which it was regenerated almost quantitatively on dilution.

10 G. of the dinitrile and 2·1 g. (1½ mols.) of anhydrous cupric chloride were heated to 260—270°; hydrogen chloride and heat were evolved and the melt solidified in 5 minutes. It was heated for a further 20 minutes at 280—290° and the green product was then extracted with water and boiling benzene. Yield of residue, 87%. Two crystallisations from chloronaphthalene gave *copper chloro*-1 : 2-*naphthalocyanine*, similar in appearance to the unchlorinated compound (Found : C, 70·7; H, 2·8; N, 13·7; Cl, 4·8; Cu, 8·0. $C_{48}H_{23}N_8ClCu$ requires C, 71·1; H, 2·8; N, 13·8; Cl, 4·4; Cu, 7·9%). The chlorine was not removed by boiling sodium hydroxide solution. 0·85 G. of the compound was dissolved in 50 c.c. of concentrated sulphuric acid, and a few drops of nitric acid added. The yellow solution yielded 0·7 g. of pale yellow solid when poured on ice, but no chloride ion. The solid melted at 250—260° after crystallisation from acetic acid and contained chlorine, but was not identified.

Zinc.—10 G. of 1 : 2-dicyanonaphthalene and 1 g. of zinc dust were heated at 275° for 20 minutes and at 310—320° for a further ¾ hour. Recovery of dinitrile, 2·3 g. Yield, 7·3 g. of a green powder with a purple lustre, containing excess of zinc. The product was slightly soluble in ether, ethyl acetate, chlorobenzene and toluene, more so in quinoline, aniline and chloronaphthalene. It was crystallised from the last-named solvent [Found : (for twice crystallised material) C, 74·9; H, 3·2; Zn, 8·3; (for thrice crystallised) C, 74·9; H, 3·2; N, 14·4; Zn, 8·4. $C_{48}H_{24}N_8Zn$ requires C, 74·1; H, 3·1; N, 14·4; Zn, 8·4%]. The solution in sulphuric acid was purple and regenerated the compound almost quantitatively on dilution.

Lead.—1 : 2-Dicyanonaphthalene (18 g.) reacted vigorously with litharge (6·8 g., 1¼ mols.) at 275—280° The mass was almost solid in 5 minutes and was heated for a further 20 minutes. The recovery of dinitrile was 3·6 g.; the yield of pigment 20·3 g., containing the excess of litharge.

Lead 1 : 2-*naphthalocyanine* was yellowish-green with a blue lustre. It was soluble in hot pyridine, quinoline, chlorobenzene, and chloronaphthalene and was crystallised from aniline (Found : C, 63·25, 63·1 *; H, 2·8, 3·0 *; N, 12·3; Pb, 21·7. $C_{48}H_{24}N_8Pb$ requires C, 62·7; H, 2·6; N, 12·2; Pb, 22·5%). 1 G. was treated with sulphuric in the usual way. Dilution yielded 0·95 g. of 1 : 2-*naphthalocyanine* contaminated with lead sulphate, from which aniline extracted the pure metal-free compound (Found : C, 80·4; H, 3·7; ash, negligible. $C_{48}H_{26}N_8$ requires C, 80·7; H, 3·6%). It was identical in appearance with the α-1 : 2-naphthalocyanine described below.

Magnesium and Metal-free Compounds.—After preliminary experiments the following procedure was adopted. 40 G. of 1 : 2-dicyanonaphthalene and 2·1 g. of etched magnesium turnings were heated at 365—370° for 80 minutes, the mass then being almost solid. The unreacted dinitrile was extracted with benzene, and the residue ground with water (this converted all the β-magnesium compound into the monohydrate, which is insoluble in ether, whereas the anhydrous β-compound appears to be slightly soluble). The product was dried and exhaustively extracted with ether (Soxhlet). Evaporation of the solution gave *α-magnesium* 1 : 2-*naphthalocyanine* as a fairly bright green mass with a fine purple lustre. A small amount of 1 : 2-dicyanonaphthalene present as impurity was sublimed out at 230—240° in a stream of carbon dioxide under reduced pressure. The *β-magnesium* 1 : 2-*naphthalocyanine* left in the extractor was sifted from excess of magnesium and again boiled with benzene. Average yields, 62% of α- and 24% of β-compound.

α-Magnesium 1 : 2-naphthalocyanine was soluble in ethyl alcohol, acetone, ethyl acetate, and chloroform and extremely soluble in ether. It was purified by two extractions with cold ether, filtration, and evaporation to dryness (Found : C, 78·3; H, 3·4; N, 15·1; Mg, 3·3. $C_{48}H_{24}N_8Mg$ requires C, 78·3; H, 3·3; N, 15·2; Mg, 3·3%). The β-isomeride was purified by two crystallisations from chloronaphthalene. Three separate preparations were analysed (Found : C, 76·4, 76·8, 76·7; H, 3·5, 3·4, 3·5; Mg, 2·9, 3·0. $C_{48}H_{24}N_8Mg,H_2O$ requires C, 76·4; H, 3·5; Mg, 3·2%).

1 G. of the α-compound was dissolved in 75 c.c. of concentrated sulphuric acid, and the purple solution filtered and poured on washed ice. The α-1 : 2-*naphthalocyanine* was washed with hot water, alcohol, and ether. Yield, 0·8 g. of a green solid with a purple lustre. It was soluble in boiling aniline but not in ether and the other low-boiling solvents which dissolved the α-magnesium compound (Found : C, 80·0; H, 3·8; N, 15·6; ash, negligible. $C_{48}H_{26}N_8$ requires C, 80·7; H, 3·6; N, 15·7%). 0·7 G. of the β-magnesium compound on similar treatment gave 0·5 g. of β-1 : 2-*naphthalocyanine*, darker green than the α-isomeride and with a purple lustre (these colours were conveniently compared as rubbings on glazed paper). It

was purified by crystallisation from chloronaphthalene (Found: C, 81·0; H, 3·7%; ash, negligible).

It seemed possible that the metal of the α-magnesium compound might be eliminated by passing dry hydrogen chloride through an ethereal solution. Experiment showed that after 2 hours the pigment was completely precipitated but only about 15% of the metal had been removed. The precipitation was caused by the formation of the oxonium compound between the ether and the hydrogen chloride, since α-magnesium naphthalocyanine was insoluble in ether saturated with the gas but dissolved when such a suspension was shaken with water.

Reactions of the Magnesium Compounds.—Metal exchange. 3 G. of α-magnesium 1 : 2-naphthalocyanine and 1 g. of reduced copper were refluxed for 36 hours in 75 c.c. of chloronaphthalene. No trace of the magnesium compound remained and the product after crystallisation from chloronaphthalene yielded pure copper 1 : 2-naphthalocyanine, identical in colour and reflex with that prepared directly from 1 : 2-dicyanonaphthalene (Found: C, 74·3; H, 3·3; Cu, 8·2%). A similar experiment with metallic zinc showed that in 7 hours about 40% of the magnesium was replaced by zinc.

Oxidation. The finely divided α-magnesium compound was heated with ceric sulphate solution until the colour was destroyed. The solution deposited 1 : 2-naphthalimide (75—80%) on standing, m. p. and mixed m. p. 224° after sublimation. A considerable excess of the theoretical amount of ceric sulphate was used up. 0·336 G. of the powdered α-magnesium compound was left in the cold for 5 days with 20 c.c. of 0·0485*N*-ceric sulphate. The yellow product was filtered from naphthalimide, and the excess of ceric sulphate estimated with ferrous ammonium sulphate in the usual way (Dent, Linstead, and Lowe, *loc. cit.*). 12·4 C.c. of ceric sulphate solution were used in the oxidation, equivalent to 1·3 atoms of oxygen per molecule (calc., 1·0).

0·5 G. of the β-magnesium compound was oxidised qualitatively in the same manner as the α-isomeride. Yield of 1 : 2-naphthalimide, 0·25 g., m. p. and mixed m. p. 224°.

Dehydration. The β-magnesium compound attained constant weight after 4 hours in a vacuum at 210—220°, the loss in weight being 2·1% (calc., 2·4%). The moisture was regained rapidly in the air and was again lost at 215°. Two separately dehydrated samples were analysed; a little hydration occurred during weighing (Found: C, 77·3, 77·4; H, 3·4, 3·4. $C_{48}H_{24}N_8Mg$ requires C, 78·3; H, 3·3%).

Reactions of the Free 1 : 2-*Naphthalocyanines.*—1 G. of α-naphthalocyanine was refluxed with granulated zinc in 30 c.c. of chloronaphthalene for 7½ hours. The pigment was purified through sulphuric acid. Analysis showed that a 46% conversion into zinc naphthalocyanine had occurred and this was practically complete after a further 24 hours' treatment. A similar reaction was performed with magnesium (24 hours), the chloronaphthalene being removed with benzene. From the residue, ether extracted the α-magnesium compound (1·3 g. from 2 g. of α-naphthalocyanine). The small portion insoluble in ether was probably the unreacted metal-free compound, but may have contained some β-magnesium compound (see below).

1·1 G. of β-1 : 2-naphthalocyanine were refluxed for 16 hours with 0·2 g. of magnesium in 40 c.c. of chloronaphthalene. The product was boiled with benzene, and the residue allowed to stand with water. Extraction with cold ether removed 0·07 g. of soluble material which appeared to be the α-magnesium derivative. The bulk of the product was insoluble (0·85 g.) and yielded the β-magnesium compound as the monohydrate after crystallisation from chloronaphthalene and standing with water (Found: C, 75·9; H, 3·6; Mg, 3·0. Calc. for $C_{48}H_{24}N_8Mg,H_2O$: C, 76·4; H, 3·5; Mg, 3·2%).

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