SUBSTITUTED PHTHALOCYANINES

A Thesis

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ABSTRACT

The preparation of a number of chloromethylated derivatives of phthalocyanine copper(II) and phthalocyanine cobalt(II) have been undertaken, and the reactions of some of these with pyridine have been investigated.

Some derivatives of phthalocyanine tin(IV) are discussed, including one which may have a 'sandwich' structure.

A new general synthetic route to alkyl substituted phthalonitriles is described, which makes use of the Diels-Alder reaction between alkyl substituted 1:3-butadienes and maleic anhydride. A number of preparative methods of these dienes have been investigated. The synthesis has been applied specifically to the preparation of 4-methylphthalonitrile, 3-methylphthalonitrile and 4:5-dimethylphthalonitrile; and from these three dinitriles have been characterised the corresponding phthalocyanines, and a series of metal derivatives.

The ultra violet and visible absorption spectra of a number of substituted phthalocyanines and some of their intermediates are included, and the effect of substitution upon line positions and intensities is discussed.

The infra red absorption spectra of the three series of methyl substituted phthalocyanines are compared with those of the unsubstituted series, and several new band assignments have been made.

The nuclear magnetic resonance spectra of three phthalocyanines are recorded and interpreted. These are dipotassium [phthalocyaninedicyanoferrate(II)] dipotassium [tetrakis-4-methylphthalocyaninedicyanoferrate(II)] and dipotassium [tetrakis-3-methylphthalocyaninedicyanoferrate(II)].

'The water, like a witch's oils,
Burnt green, and blue, and white.'

Samuel Taylor Coleridge.

To **ANGELA**

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INTRODUCTION

The phthalocyanines are no longer regarded as novel compounds, for they have been established by thirtyfive years of study, and have achieved a wide variety of applications, both inside and outside the chemical industry. Their fourfold properties of high thermal stability, insolubility, intense colour and fastness to light, have brought them a certain notoriety, and in many respects, they are not easy compounds to handle. However, they make excellent pigments for plastics, paper and paints, and every month details of new solublised phthalocyanine dyes appear in the literature. They have been shown to catalyse a number of chemical reactions; they exhibit semi-conductor properties; they have provided useful models in certain x-ray crystallographic measurements, and they have been used to demonstrate perpendicular conjugation - the transference of electronic charge between two perpendicular planes.

Although these points go some way towards demonstrating the versatility of the phthalocyanines, there are still a number of gaps in the work that has been published on them. For example, most substituted phthalocyanines are prepared by direct substitution of the pigments by various reagents, this type of reaction being rather random, and difficult to control. There are very few references in the literature to the preparation of substitution products by the cyclisation of substituted derivatives of phthalic acid, although this method has the advantage of introducing a known number of groups into predetermined positions. The infrared data available on the unsubstituted pigments are good and comprehensive but few band assignments have been made, and there are little data available on derivatives with peripheral substituents. Finally, no nuclear magnetic resonance measurements have been made on phthalocyanines in solvents other than concentrated sulphuric acid, in view of their low solubility.

The initial purpose of this work had been to attempt a systematic study of the direct chloromethylation of certain phthalocyanines, in the hope of obtaining from the products, water-soluble pyridinium salts of known configuration. Although fifteen new compounds were prepared, it was quickly realised that this approach was unsatisfactory, since both the nature of the products, and the yields were found to depend on too many factors. Attention was turned briefly to the direct substitution of phthalonitrile, and then to the search for a general synthetic route to substituted phthalonitriles. Such a route has been found, by making use of the Diels-Alder reaction between substituted butadienes and maleic anhydride, and subsequent conversion of the adduct to the aromatic dinitrile. Although this generally results in alkyl substituted products, these may be converted to other derivatives by oxidation, halogenation etc.

The route depends for its success upon the availability of substituted dienes, and a number of synthetic routes to these have been investigated, and others are discussed. The diene synthesis has been successfully applied to the preparation of 4-methylphthalonitrile, 3-methylphthalonitrile, and for the first time, 4:5-dimethylphthalonitrile. From these dinitriles, three new series of phthalocyanines have been prepared, and the physical, and visible and infrared spectroscopic properties of about twentyfive derivatives are recorded. A careful study of the effect of methyl substituents upon the infrared spectra of the phthalocyanines has led to the assignment of a number of new bands, and a useful method for distinguishing the substitution pattern around the periphery of the ring has been discovered. Finally, by making use of the reaction between potassium cyanide and phthalocyanine iron(II), to give a product very soluble in methanol, nuclear magnetic resonance measurements have been made on three phthalocyanines, and the positions of the lines have confirmed the aromatic nature of the tetrazaporphin ring.

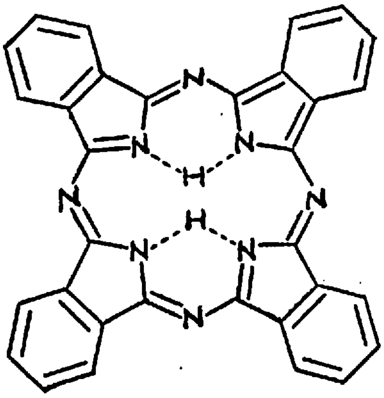
CHAPTER I

THE CHLOROMETHYLATION OF PHTHALOCYANINES

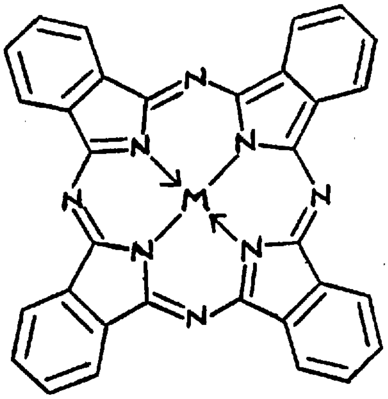
A. Introduction

The earliest record of what must undoubtedly have been a phthalocyanine was made by Braun and Tcherniac(1) in 1907, who observed a blue colour on fusing o-cyanobenzamide. In 1927, phthalocyanine copper (II) and two of its derivatives were produced by de Diesbach and von der Weid(2) as byproducts in an attempt to prepare aromatic o-dinitriles. They mistakenly identified these blue pigments as complexes between the dinitriles, pyridine and copper, and were astounded and puzzled by their tremendous stability. "We would be happy if those more specialised in the study of complex salts would throw some light on the structure and causes of stability in these new products". It was a year later that a blue colour observed during the preparation of phthalimide at the Grangemouth works of Messrs. Scottish Dyes Limited led to the isolation of phthalocyanine iron (II) and subsequently to the work of Linstead and his co-workers in the early 1930's(3)(4)(5)(6)(7)(8). They prepared the parent compound phthalocyanine (PcH_2)(4), a number of metal derivatives(5) and elucidated their structures as I and II(8). These results were later confirmed by X-ray crystallographic work(9)(10)(11)(12).

In view of their strong colour, great stability and fastness to light, the potentialities of these compounds as pigments was



I



II

quickly realised, and this is borne out by the number of preparative methods that soon appeared in the patent literature(13)(14)(15)(16)(17)(18). In these methods, the pigments are prepared by heating phthalic derivatives, such as the anhydride, imide, diamide or o-cyanobenzamide, with ammonia, with or without a metal or metal derivative. Later work(16) favoured the reaction between phthalonitrile and a metal, or metal derivative, as this tended to go more easily, and in higher yields.

Excellent pigments, as they are, the phthalocyanines are exceedingly insoluble in all but the highest boiling solvents, such as 1-chloronaphthalene and quinoline; and hence are of little use in dyeing fabrics. However, work such as that at I.G. Farbenindustrie(19), showed that solublised derivatives suitable for dyeing cellulose fabrics could be prepared by sulphonation of e.g. phthalocyanine copper(II) (Cu Pc) with 40% oleum, and subsequent reaction with organic bases. In the late 1940's the Friedel-Crafts type of reaction was used with great success in the incorporation of chloromethyl groups into the phthalocyanine ring, and further reaction with nitrogen and sulphur bases, yielded a wide range of soluble dyes(20)(21)(22)(23)(24)(25). Later work extended the reaction to the incorporation of up to eight N-methylene phthalimido groups, and hence eight aminomethyl groups(26), and these were quaternised with a wide variety of organic acids to produce further soluble dyes. So the field has expanded.

In view of the insolubility of the compounds, little effort was made in the above work to separate and identify the necessarily large number of different products and isomers resulting from substitution reactions, more emphasis being laid on obtaining reproducible results. Therefore, it was felt that it would be useful to make a systematic study of the chloromethylation of some phthalocyanines, and the subsequent quaternisation of the products with pyridine, in order to establish any relationship between degree and orientation of substitution, solubility and spectroscopic data. It was also hoped that the hitherto unrecorded heptakis and octakis-chloromethyl derivatives might be prepared.

B. Phthalocyanine Copper (II)

Phthalocyanine copper (II) has been recorded in the literature, substituted with anything from one to six chloromethyl groups, e.g.(20)(22). The phthalocyanine ring has sixteen positions in which substitution might take place, four on each o-phenylene ring. Eight of these positions, however, namely the 3 and 6 positions on each ring, are more sterically hindered than the other eight, the 4 and 5 positions; and thus, as Lacey(26) points out, substitution with bulky groups, as in the Friedel-Crafts reaction, will cease when eight groups have been introduced. Apparent anomalies, such as the tetrakis-4-phenyl-octakis-chloromethyl phthalocyanine copper (II), described by Haddock and Wood(22)(23) actually have at least four of the chloromethyl groups attached to the 4-phenyl substituents, and a maximum of four attached to the phthalocyanine ring.

Wood(25) describes the chloromethylation of phthalocyanine cobalt (II) by heating the pigment in an aluminium chloride-pyridine eutectic containing 1:1'-dichlorodimethyl ether; the degree of chloromethylation depending on the concentration of chloro ether, the temperature of the melt, and the heating time. This is the method which was used in this work, suitably modified for the use of phthalocyanine copper (II) and for higher degrees of chloromethylation. Very finely milled Cu Pc was used (I.C.I. Monastral Fast Blue B.S. Powder) and in view of the expensive nature of the chloroether, reactions were carried out on the 0.5 - 2.5 g scale (on Cu Pc).

It very soon became apparent that a large number of factors governed the nature and the yield of the products from this reaction. This is best illustrated in Table I, which gives a correlation between experimental conditions, yields and degree of chloromethylation.

Table I

Run	No. of groups substituted	Ratio $CuPc/CH_2Cl)_2O$	Scale 1≡CuPc 0.8g	Heating time	Temperature (°C)	Yield %
1	3 - 4	1 : 2.0	1.0	90 mins	75 - 82°C	4.5
2	5	1 : 0.75	2.5	30 mins	55 - 60°C	4.6
3	5	1 : 0.9	2.0	30 mins	55 - 60°	4.7
4	~ 6	1 : 2.2	2.0	180 mins	82 - 88°C	3.9
5	6?	1 : 0.8	0.5	30 mins	55°C	8.8
6	6?	1 : 0.8	2.0	30 mins	62°C	3.4
7	7	1 : 2.7	0.5	120 mins	70 - 78°C	37.5
8	7	1 : 2.9	0.5	120 mins	95 -100°	-
9	8	1 : 2.4	1.0	150 mins	90 - 92°C	10.6
10	8	1 : 2.2	2.5	180 mins	86 - 88°	17.1
11	8	1 : 1.8	2.6	180 mins	88 - 92°C	5.8

To supplement these data, it must be added that in runs 1, 7 and 8 an old stock of $(CH_2Cl)_2O$ was used, whereas the remainder made use of a fresh batch. Also in runs 10 and 11 partly chloromethylated Cu Pc (1 - 2 groups) was used in place of the pure pigment. In one of two additional runs, not listed, the reactants were scrupulously dried before use, and in the other a small quantity of water was deliberately added. In both cases the yield was extremely small. From these results, the following points can be made with regard to this chloromethylation reaction :

1. Smaller scale reactions tend to give better yields, due to more efficient stirring.
2. Yields improve with longer heating time, but the temperature heating time relationship for a particular product seems to be quite critical.
3. The most critical factor of all seems to be the quantity of water in the system. Although the best results were obtained if fresh chemicals were weighed straight from the bottles, and exposed to the air for as little time as possible, the yields were none the less affected considerably by the humidity of the air on the particular day.
4. During the work-up of the product with water, a violent exothermal reaction takes place, accompanied by hydrolysis of some of the chloromethyl groups, e.g. the products of runs 2, 3, 5 and 6 all contain oxygen. In order to prevent hydrolysis, it was found necessary to use crushed ice in place of water.

<u>Run 1</u>

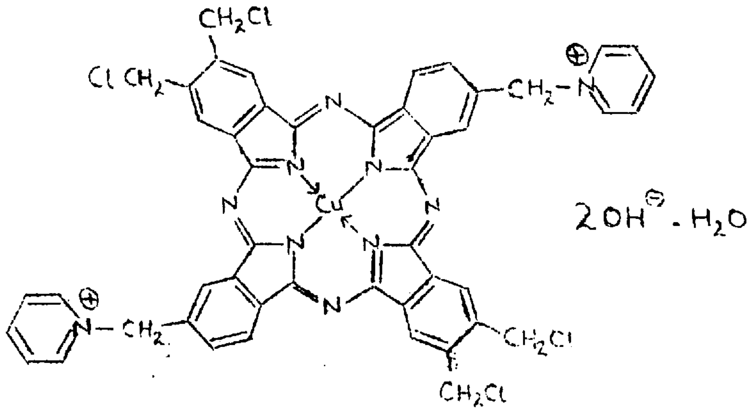
This yielded a product which analysed between Cu Pc $(CH_2Cl)_3$ and Cu Pc $(CH_2Cl)_4$. Chromatography on kieselguhr and on tartaric acid, using benzene as an eluent failed to separate the mixture into its components. This observation was found to be a general rule where substituted phthalocyanines containing a similar number of identical substituents were concerned.

Runs 2 and 3

These two runs were reproducible in themselves, but it must be pointed out that they were carried out in an attempt to repeat the products of runs 5 and 6. In fact the product of run 3 gave a similar analysis to those from 5 and 6, but its visible spectrum was appreciably different, being identical with that of the product from run 2. A further point is that the ignition residues from 2 and 3 analysed as CuO, whereas those from 5 and 6 analysed as $CuCl_2$. This point will be discussed in more detail later.
The products were identified as bis chloromethyl - tris hydroxymethylphthalocyanine copper (II), Cu Pc $(CH_2Cl)_2(CH_2OH)_3$, the hydroxyls being introduced as a result of hydrolysis on work-up.

Run 4

The hexakischloromethylphthalocyanine copper(II) Cu Pc $(CH_2Cl)_6$, from this run was not obtained analytically pure. However, on heating a sample with pyridine in a sealed tube at 117°C, a product was isolated, which analysed as : Cu Pc $(CH_2Cl)_4(CH_2Py^{\oplus})_2$ $2OH^{\ominus}.H_2O$ the water coming from traces in the pyridine. In view of later discussion, it is worth commenting here that the residue from ignition of this compound analysed as CuO. It is difficult to predict where the hydroxyl ions will fit into the crystal lattice of this compound, and although there is some evidence that they may be loosely bonded to the copper atom, above and below the plane of the ring, this is by no means certain. The following structure is suggested, the positions of quaternisation being chosen as the least sterically hindered :

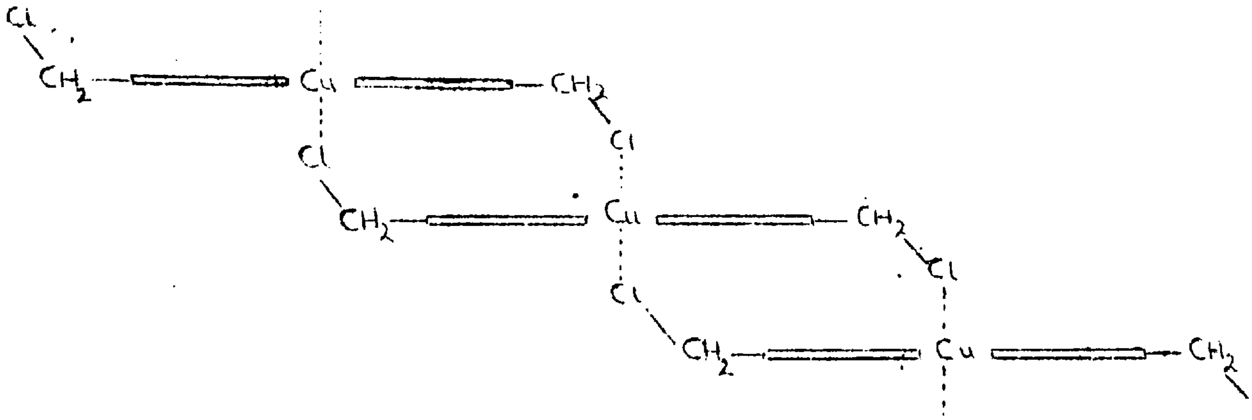


Runs 5 and 6

The products of these two runs must remain a mystery until further work can be carried out. Within experimental error, the analyses are identical :-

C = 60.84, H = 3.37, N = 15.20, Cl = 9.46, O = 2.45
C = 60.92, H = 3.24, N = 14.96, Cl = 10.36, O = 2.53 %

No satisfactory structure can be derived to fit these results, bearing in mind the experimental conditions. Treatment of a sample with PCl_5 in benzene yielded a compound containing 11.41% Cl, whereas treatment with 10% NaOH increased the oxygen content to 4.34%. No deductions could be made from these results. Both samples on ignition in air yielded a residue of cupric chloride instead of the expected oxide, which raised further questions. This effect, in which $CuCl_2$ is isolated as an ignition residue was first observed during the analysis of the dipyridinium derivative of CuPc $(CH_2Cl)_8$, obtained as a product from run 10. At first it was thought that the two chloride ions from the quaternisation were weakly bonded to the copper atom, as a result of the electron withdrawing properties of the chloromethyl and pyridinum groups. Ignition of such a compound would be more inclined to give $CuCl_2$ as a residue, and this may in fact be what is happening to this pyridinum salt. A more general explanation, however, which would account for the observance of this result with non-quaternised chloromethylated phthalocyanines, such as the two under discussion (see also section C, cobalt (II) phthalocyanines) is as follows. The joint negative inductive effects of several chloromethyl groups in a phthalocyanine would be expected to reduce the electron density at the copper atom, and this could be offset if the molecules packed in the following manner in the crystal lattice :



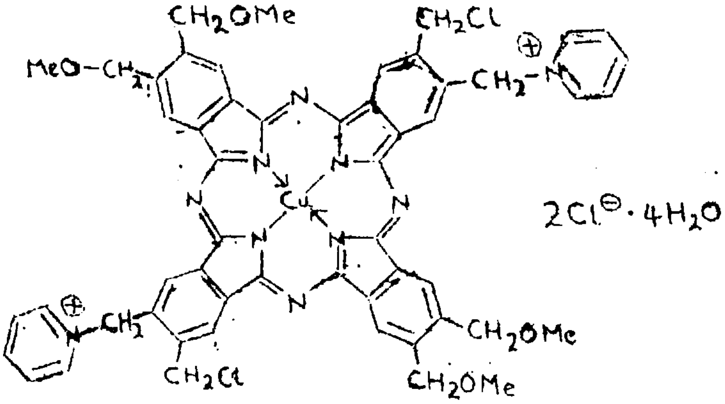
The phthalocyanine rings are at right angles to the plane of the paper. The nature of the ignition residue would thus depend on the ability of the phthalocyanine, whether quaternised or not, to form such a lattice. This would help to explain some of the apparently anomalous results discussed later.

Runs 7 and 8

The second of these runs produced an analytical sample of *heptakischloromethylphthalocyanine copper (II)* $Cu\ Pc\ (CH_2Cl)_7$, which, unlike lower chloromethylated derivatives, must exist as a single isomer. The product from the first run, though not quite so pure, was still the highest yield from any chloromethylation of phthalocyanine copper (II). A sample of $Cu\ Pc\ (CH_2Cl)_7$ heated on a steam bath with pyridine, yielded a dipyridinium dichloride tetraethanolate $Cu\ Pc\ (CH_2Cl)_5(CH_2Py^{\oplus})_2.2Cl^{\ominus}.4\ EtOH$ after recrystallisation from benzene/ethanol. The positions of the bands in the visible spectrum of this compound, before and after recrystallisation, are identical, and their extinction coefficients are also identical on the assumption that before recrystallisation the product was $Cu\ Pc\ (CH_2Cl)_5(CH_2Py^{\oplus})_2.2Cl^{\ominus}$. A second sample was refluxed with pyridine overnight, and the product after recrystallisation from alcohol, and drying under vigorous conditions, proved to be the tripyridination salt, $Cu\ Pc\ (CH_2Cl)_4(CH_2Py^{\oplus})_3.3Cl^{\ominus}$. It was found to be very soluble in water, methanol and ethanol; soluble in isopropanol; slightly soluble in tertiary butanol, and insoluble in benzene and acetone. It thus appears that tripyridinum salts can be formed, but the conditions are necessarily more vigorous. The ignition residue of none of these compounds was examined.

Run 9

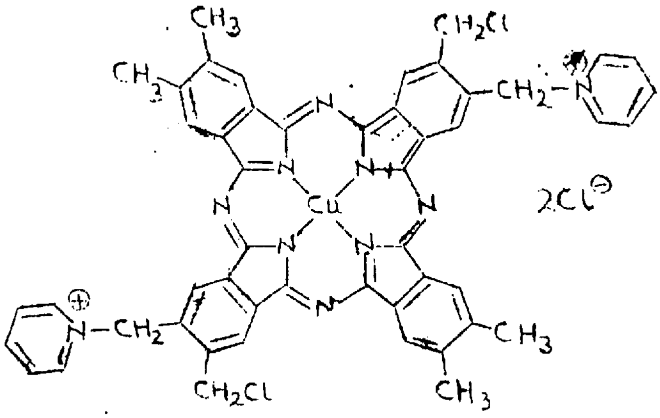
The analytical sample of *octakischloromethylphthalocyanine Copper (II)*, $Cu\ Pc\ (CH_2Cl)_8$, isolated in this run, was found to be quite appreciably more soluble in benzene than the heptakischloromethyl derivative. An attempt was made to quaternise more than four of the chloromethyl groups with pyridine, by refluxing a sample in pyridine, and then refluxing the precipitated product overnight with a mixture of pyridine and methanol. After drying, the product analysed either as $\underline{\mathrm{Cu\ Pc\ (CH_2Cl)_2(CH_2OH)_4(CH_2Py^{\oplus})_2.2Cl^{\ominus}.3MeOH}}$, or as $\underline{\mathrm{Cu\ Pc\ (CH_2Cl)_2(CH_2OMe)_4(CH_2Py^{\oplus})_2.2Cl^{\ominus}.4H_2O}}$. The former product fits the analysis more closely, but the latter seems more likely in view of the experimental conditions. The ignition residue analysed as $CuCl_2$, and the following structure may be proposed :



Although this molecule had been subjected to refluxing methanol under basic conditions overnight, only four chloromethyl groups have been attacked (to give alcohols or methoxyls). It thus appears that the remaining two are protected in some way, and this only seems reasonable if they are adjacent to the pyridinum groups as shown. One may postulate a weak electrostatic bond between the positively charged pyridine nuclei, and the covalent chlorines, and if this were the case, the two chloromethyl groups would be in an unfavourable orientation for Sn2 attack from above or below the plane of the phthalocyanine ring. Such a hypothesis has little other than circumstantial evidence to support it. If the formation of $CuCl_2$ on ignition is to be explained, one has to fit the chloride ions into the lattice above and below the copper atoms, which in this case is not unreasonable.

Runs 10 and 11

Extraction and purification of chloromethylated derivatives with benzene always leaves a benzene insoluble residue of phthalocyanine, containing about two chloromethyl groups. In these two runs use was made of such residues, on the assumption that they would be more soluble in the $AlCl_3$/pyridine eutectic and should be completely chloromethylated more readily, thus increasing the yields of the octakischloromethyl compound. This was successful in run 10, but not in run 11, and spectroscopically the two products were identical with that from run 9. Quaternisation was attempted by heating a sample with dry pyridine in a Carius tube. Three temperatures were tried, namely 195°, 150° and 115° but only in the latter case was an identifiable product isolated. This compound analysed as $C_{50} H_{38} N_{10} Cl_4 Cu$, and the residue after ignition as $CuCl_2$. Examination of this formula shows that once again only four chloromethyl groups have been attacked, once two have been quaternised; and this time they have apparently been reduced (perhaps by traces of piperidine) to methyl groups. Using the arguments outlined in the last section, it is reasonable to propose the following structure for this compound, and there is no reason why the positions of the two chloride ions should be any different :



$\underline{Me_4\ CuPc\ (CH_2Cl)_2(CH_2Py^{\oplus})_2.2Cl^{\ominus}}$

C. Phthalocyanine cobalt <u>(II)</u>

There are few references to the chloromethylation of phthalocyanine cobalt (II) in the literature, e.g.(25), but in view of the inconsistent results obtained from phthalocyanine copper (II) and bearing in mind the greater solubility of the cobalt derivative attention was turned here. The parent compound was prepared by heating together an intimate mixture of anhydrous cobalt chloride and phthalonitrile at 200°, yielding 72% of the pigment. This was later found to be contaminated with a chloro derivative (see

Barrett, Dent and Linstead(27)), so the preparation was repeated using anhydrous cobalt acetate in place of the chloride. The yield of analytical pigment was 65%.

Using quantities and conditions exactly as in the first successful preparation of $\mathrm{CuPc(CH_2Cl)_8}$, only making use of a shorter heating time, octakischloromethylphthalocyanine cobalt (II) $\mathrm{CoPc(CH_2Cl)_8}$ was isolated in 25% yield. Fractional crystallisation of this compound separated it into two components, one very much more soluble in benzene than the other. Both samples, however, analysed as $\mathrm{CoPc\ (CH_2Cl)_8}$, but the ignition residue from the larger sample proved to be cobaltous oxide, and that from the smaller, cobaltous chloride. It seems likely that these two samples are different crystalline forms of the same material, particularly as their absorption spectra are identical. The second sample, which gave an ash of $\mathrm{CoCl_2}$ may well have a crystal lattice built up in much the same way as that illustrated on page 22, which would explain the lower solubility, in view of the higher lattice energy; and also the formation of $\mathrm{CoCl_2}$ on ignition. The more soluble form would presumably be packed more loosely. The preparation was repeated in 31% yield, the ignition residue from this sample analysing as $\mathrm{CoCl_2}$. Quaternisation of this material by refluxing with pyridine for 3 hours yielded a compound which analysed as $\mathrm{C_{50}\ H_{49}\ N_{10}\ Cl_7\ O_8\ Co}$. On the assumption that it is a dipyridinium salt, its structure would be :

$$\underline{\mathrm{CoPc\ (CH_2Cl)_6(CH_2Py^{\oplus})_2\ OH^{\ominus}\ Cl^{\ominus}.7H_2O}}\ .$$

It is not certain whether the OH is present as a hydroxide ion or as a covalently bonded substituent. The ignition residue analysed as $CoCl_2$. This sample was dried at 120°, 0.01 mm to give the anhydrous material, $\underline{\mathrm{CoPc\ (CH_2Cl)_6(CH_2Py^{\oplus})_2\ OH^{\ominus}\ Cl^{\ominus}}}$. Unfortunately as with all phthalocyanine pyridinum salts prepared, attempts to obtain infra red data were unsuccessful. The salts would not mull with nujol, and potassium chloride discs showed very broad diffuse bands with high background, due to scattering effects. Although many of the salts were very soluble in methanol, nuclear magnetic resonance studies were equally futile, since both copper and cobalt in a square planar configuration have one unpaired electron.

A second sample was sealed in a tube with pyridine and heated overnight at 123°. The product analysed as $C_{50}\ H_{50}\ N_{10}\ Cl_6\ O_9\ Co$, the ignition residue analysing as $CoCl_2$. By analogy with the product previously isolated, this was given the structure $\underline{\mathrm{CoPc\ (CH_2Cl)_6(CH_2Py^{\oplus})_2.2OH^{\ominus}.7H_2O}}$, but it must be emphasised that the positions and nature of the hydroxyls are uncertain. Unfortunately there was insufficient of this material available to allow further studies.

No attempt was made to prepare further chloromethylated derivatives of phthalocyanine cobalt (II) as it was realised at this stage that a more systematic approach might be the preparation of mono- and bis-chloromethyl phthalonitriles, and subsequent cyclisation of these compounds to give products of known configuration. However, before this approach was abandoned, a brief study was made of the chloromethylation of metal-free phthalocyanine, PcH_2.

D. Phthalocyanine

In their original patent on this subject, Haddock and Wood$^{(20)}$ refer to the chloromethylation of both CuPc and PcH_2 using $(CH_2Cl)_2O$ in an aluminium chloride/pyridine eutectic. Later patents e.g.$^{(28)}$ use paraformaldehyde and chlorsulphonic acid as the reagents. In this work, the former method was used as a parallel to the studies made on CuPc and CoPc. Several runs were carried out, but on each occasion the product was contaminated by a considerable quantity of yellow brown tarry material. Attempts to remove this by stirring with solvents such as benzene, methanol or acetone, resulted in the chloromethylated phthalocyanine being drawn into solution also. Chromatography failed to bring about a separation, as alumina absorbed both materials very strongly, and tartaric acid failed to hold either. The starting material (I.C.I. Monastral Fast Blue G.S. Powder) was recrystallised to yield an analytical sample, but this also gave a tarry product after chloromethylation. A study of the visible absorption spectra of these derivatives showed a pattern of bands of the same form as those of PcH_2, but shifted to longer wavelengths, as would be expected (see Chapter 10), Quaternisation with pyridine yielded highly water soluble products, confirming that chloromethylation had taken place, and this was further confirmed by analysis, which showed a high percentage of chlorine. However, a residue of ash always remained after combustion of these compounds, and a flame spectrum of the ash showed it to contain aluminium and silicon. This metal residue was shown to come from the pigment, and not the tar, by preparing a large quantity of chloromethylated derivative, removing all traces of tar by scrupulous washing with methanol (with great loss of pigment), and analysing the product after careful drying. It appeared to be a mixture of *octakischloromethylphthalocyanine* and *octakischloromethylphthalocyanine hydroxy-aluminium*, $PcH_2(CH_2Cl)_8$ and $Al(OH)Pc(CH_2Cl)_8$, and thus it seems that the $AlCl_3$ method is unsuitable for the chloromethylation of phthalocyanine.

E. Experimental section

The numbers in parentheses refer to the number(s) of the preparations, occurring in the notebooks. Unless otherwise stated, all analyses in this thesis were carried out in the Organic Chemistry Department Microanalytical Laboratories under the direction of Miss Cuckney.

Tris and tetrakischloromethylphthalocyanine copper (II) (6)

Anhydrous $AlCl_3$ (4.8 g, finely crushed) was added to pyridine (1.2 g, G.P.R.) in a 25 ml three necked flask, and the mixture heated at 150° with vigorous stirring on an oil bath for 1 hour. The stirrer was stopped, the flask allowed to cool to 60°, dichlorodimethyl ether (1.6 g) added, and the stirrer started. Cooling was continued until 45° had been reached, when phthalocyanine copper (II) (0.8 g) was added, and the temperature increased to 75 - 82° for 90 mins. The product after working up with ice, was washed well with water, dried at 80°, and three times extractionally crystallised from benzene on a soxhlet.

Yield 42 mg, 4.5%

Calc. for CuPc $(CH_2Cl)_3$: C = 58.25; H = 2.65; Cl=14.75; N=15.53

Calc. for CuPc $(CH_2Cl)_4$: C = 56.18; H = 2.62; Cl=18.41; N=14.55

Found : C = 57.11; H = 3.71; Cl=18.94; N=12.77%

These data are taken as standard for all following chloromethylations being defined as scale 1. This refers to 0.8 g CuPc as compared with 4.8 g $AlCl_3$. Conditions for all following runs are identical up to the addition of CuPc, and unless otherwise stated, products were all worked up and purified as above.

Bis-chloromethyl-tris-hydroxymethylphthalocyanine copper (II) (25)(26)

Scales 2.5 and 2.0. In both cases $(CH_2Cl)_2O$ (1.2 g) was used, a second addition (0.2 g) being made when the maximum temperature had been attained. Heating was continued at 55 - 60° for 30 min. The product was worked up and purified as before.

Yields : 92 mg, 4.6%; 84 mg, 4.7%

$C_{37}H_{24}Cl_2CuN_8O_3$ requires :

C = 58.19; H = 3.17; Cl = 9.32; N = 14.69; O = 6.30

Found : C = 58.41; H = 3.18; Cl = 9.84; N = 14.75; O = 6.22

Found : C =(61.01);H = 3.03; Cl = 9.24; N = 14.72 %

The ignition residue analysed as CuO.

Hexakischloromethylphthalocyanine copper (II) (16)

Scale 2.0. $(CH_2Cl)_2O$ (3.5 g) was used, and heating continued at 82 - 88° for 180 min.

Yield : 70 mg, 3.9%

Calc. for $C_{38} H_{22} Cl_6 Cu N_8$:

C = 52.61; H = 2.56; Cu = 7.33

Found : C = 51.92; H = 3.34; Cu = 7.40 %

The ignition residue analysed as CuO.

Dipyridinium derivative (23)

Hexakischloromethylphthalocyanine copper (II) (40 mg) was dissolved in pyridine (10 ml G.P.R.) and sealed in a Carius tube. It was heated at 117° for 18 hours and the product filtered off and dried at 100°, 15 min.

$C_{48} H_{36} Cl_4 Cu N_{10} O_3$ requires :

C = 57.31; H = 3.60; Cl = 14.09; N = 13.92

Found : C = 57.49; H = 4.14; Cl = 14.11; N = 14.04 %

Ignition residue analysed as CuO.

Products from runs 5 and 6 (20)(21)

Scales 0.5 and 2.0. $(CH_2Cl)_2O$. (0.3 g and 1.2 g respectively) was used, and heating continued for 30 min at 55° and 62°.

Yields 50 mg, 8.8% and 77 mg, 3.4%

Run 5 C = 60.84; H = 3.37; Cl = 9.46; N = 15.20; O = 2.45

Run 6 C = 60.92; H = 3.24; Cl = 10.36; N = 14.96; O = 2.53 %

The ignition residues analysed as $CuCl_2$

Heptakischloromethylphthalocyanine copper (II) (1)

Scale 0.5. $(CH_2Cl)_2O$ (0.8 g) was used, and heating continued for 120 min at 70 - 78°.

Yield 205 mg, 37.5%

$C_{39}H_{23}Cl_7CuN_8$ requires :

C = 51.1; H = 2.53; Cl = 27.10

Found : C = 52.20; H = 3.13; Cl = 27.35 %

Dipyridinium tetra ethanolate (2)

50 mg heptakischloromethylphthalocyanine copper (II) was dissolved in pyridine (10 ml) and heated on a steam bath at 100° for 2 hours. The product was filtered off and recrystallised from ethanol.

$C_{57}H_{57}Cl_7CuN_{10}O_4$ requires :

C = 54.45; H = 4.56; Cl = 19.74; N = 11.14

Found : C = 55.51; H = 4.29; Cl = 19.44; N = 11.05 %

Heptakischloromethylphthalocyanine copper (II) (3)

Scale 0.5. $(CH_2Cl)_2O$ (0.8 g) used, and heating continued at 95 - 100° for 120 min.

$C_{39}H_{23}Cl_7CuN_8$ requires :

C = 51.10; H = 2.53; Cl = 27.10

Found : C = 51.09; H = 3.25; Cl = 27.62 %

Tripyridinium derivative (7)

50 mg heptakischloromethylphthalocyanine copper (II) was dissolved in a large excess of pyridine (dried over BaO) and

heated under reflux for 17 hours. The product was filtered off, taken up in EtOH, filtered, evaporated under reduced pressure, and dried at 100°, 0.01 mm over P_2O_5 for 17 hours.

$C_{54}H_{38}Cl_7CuN_{11}$ requires :

C = 56.25; H = 3.32; N = 13.42

Found : C = 56.74; H = 4.76; N = 13.29 %

Octakischloromethylphthalocyanine copper (II) (10)

Scale (1) $(CH_2Cl)_2O$ (1.6 g) used and heating continued for 150 min at 90 - 92°.

Yield 140 mg, 10.6%

$C_{40}H_{24}Cl_8CuN_8$ requires :

C = 49.86; H = 2.51; Cl = 29.42; N = 11.62

Found : C = 49.89; H = 2.82; Cl = 29.41; N = 11.60 %

Dipyridinium methoxyhydrate or hydroxymethanolate (11)

Octakis chloromethylphthalocyanine copper (II) (110 mg) was heated under reflux for 1 hour with pyridine (15 ml, dried over BaO). The product was filtered off, taken up in a mixture of methanol (7 ml) and pyridine (10 ml) and heated under reflux overnight. The product was evaporated to dryness under reduced pressure, taken up in methanol/water, filtered, evaporated under reduced pressure and dried over night (80° 0.1 mm).

$CuPc\,(CH_2OMe)_4(CH_2Cl)_2(CH_2Py^{\oplus})_2\cdot 2Cl^{\ominus}\cdot 4H_2O$ requires :-

C = 55.12; H = 4.62; Cl = 12.06; N = 11.91; O = 10.89

$CuPc\,(CH_2OH)_4(CH_2Cl)_2(CH_2Py^{\oplus})_2\cdot 2Cl^{\ominus}\cdot 3MeOH$ requires :-

C = 55.62; H = 4.40; Cl = 12.39; N = 12.25; O = 9.79

Found : C = 55.58; H = 4.70; Cl = 12.17; $\left\{\begin{array}{l} N = 11.90 \\ N = 12.34 \end{array}\right\}$ O = 9.44 %

Octakischloromethylphthalocyanine copper (II) (17)(18)

Scales 2.4 and 2.6. Partly chloromethylated CuPc, containing ~ 2 chloromethyl groups, residue from earlier reactions, was used in place of unsubstituted CuPc. $(CH_2Cl)_2O$. (4.4 and 3.4 g respectively) was used and heating continued for 180 min at 86 - 88° and 88 - 92°. Yields 620 mg, 17.1% and 200 mg, 5.8%.

$C_{40} H_{24} Cl_8 Cu N_8$ requires :

C = 49.86; H = 2.51; Cu = 6.59;

Found : C = 48.33; H = 3.04; Cu = 7.40

Found : C = 49.58; H = 2.95; Cu = 6.59 %

The ignition residue analysed as CuO

Dipyridinium tetramethyl derivative (19)

Octakischloromethylphthalocyanine copper (II) (200 mg) was dissolved in pyridine (25 ml dried over BaO) and heated for 18 hours at 115°. The product was filtered off and dried (100°, 15 mm).

$CuPc\ (Me_4)(CH_2Cl)_2(CH_2Py^{\oplus})_2.\ 2Cl^{\ominus}$

$C_{50} H_{38} Cl_4 Cu N_{10}$ requires :

C = 61.09; H = 3.89; Cl = 14.42; Cu = 6.46; N = 14.25

Found : C = 61.55; H = 4.52; Cl = 14.58; Cu = 6.50; N = 14.32 %

The ignition residue analysed as $CuCl_2$.

Octakischloromethylphthalocyanine cobalt (II) (34)(35)

The same method of preparation was used as in the successful synthesis of CuPc $(CH_2Cl)_8$. $(CH_2Cl)_2O$ (1.8 g) was added to a melt of $AlCl_3$ (4.9 g) and pyridine (1.3 g); CoPc (0.8 g) added at 45° and the mixture heated with vigorous stirring at 85 - 90° for 45 min. The product was worked up in the usual fashion, yielding after three extractional crystallisations from benzene 300 mg, 22% of the more soluble form, and 40 mg, 3% of the less soluble form. The ignition residue from the larger sample analysed as CoO and that of the smaller as $CoCl_2$.

$C_{40}H_{24}Cl_8CoN_8$ requires :

C = 50.08; H = 2.52; Cl = 29.57; Co = 6.15; N = 11.68

Found : C = 50.25; H = 2.75; Cl = 29.58; Co = 6.09; N = 11.41

Found : C = 49.72; H = 2.49; Co = 7.0; N = 11.46%

Dipyridinium hydroxychloride heptahydrate (36)

100 mg of CoPc $(CH_2Cl)_8$ was refluxed with pyridine (20 ml) for 3 hours. It was filtered off and dried at 100°, 15 mm.

$C_{50}H_{49}Cl_7CoN_{10}O_8$ requires :

C = 48.97; H = 4.03; Cl = 20.22; Co = 4.81; N = 11.44; O=10.43

Found : C = 49.03; H = 4.58; Cl = 13.86; Co = 5.3; N = 11.59; O=10.47 %

The ignition residue analysed as $CoCl_2$. The chlorine analysis gave considerable trouble, neither the ignition method nor the gravimetric method being satisfactory. The above figure was obtained by ignition, which left a residue of CoO and $CoCl_2$ after a long combustion. The gravimetric method gave a silver/cobalt complex .

Dipyridinium hydroxychloride (44)

The above heptahydrate was dried for 2 hours at 120°, 0.01 mm.

$C_{50} H_{35} Cl_7 Co N_{10} O$ requires :

C = 54.62; H = 3.23; N = 12.74; O = 1.46

Found : C = 54.16; H = 3.06; N = 12.58; O = 1.40 %

The ignition residue was not examined.

Octakischloromethylphthalocyanine cobalt (II) (37)

Conditions and quantities were used exactly as in the successful preparation above, except that a second addition of chloro ether (0.3 g) was made after the CoPc had been added and heating was continued at 80 - 85° for 60 min.

Yield 410 mg, 30.6%.

$C_{40} H_{24} Cl_8 Co N_8$ requires :

C = 50.08; H = 2.52; Cl = 29.57; Co = 6.15; N = 11.68

Found : C = 50.07; H = 2.60; Cl = 31.78; Co = 7.2; N = 10.81 %

The ignition residue analysed as $CoCl_2$.

Dipyridinium dihydroxide heptahydrate (47)

100 mg CoPc $(CH_2Cl)_8$ was dissolved in pyridine (10 ml) and sealed in a soda glass tube. This was suspended for 17 hours in the boiling vapour of 2-methyl pentanol at 123°. The product was filtered off and dried.

$C_{50} H_{50} N_{10} Cl_6 O_9 CO$ requires :

C = 49.81; H = 4.17, Co = 4.88; N = 11.61; O = 11.93

Found : C = 49.80; H = 3.13; Co = 4.76; N = 10.46; O = 11.83 %

The ignition residue analysed as $CoCl_2$.

Chloromethylation of phthalocyanine (31)

$(CH_2Cl)_2O$ (3.2 g) was dissolved in a melt of $AlCl_3$ (9.7 g) and pyridine (2.4 g), and PcH_2 (1.4 g) added at 45°. The mixture was heated at $85 - 90^\circ$ for 30 min, cooled, worked up with ice, washed well with water and dried. The green, pitch-like material was washed well with methanol and twice recrystallised from benzene in a soxhlet.

$Al(OH)Pc(CH_2Cl)_8$.

$C_{40}H_{25}AlCl_8N_8O$ requires :

C = 51.44; H = 2.70; Cl = 29.26; N = 12.00

$PcH_2(CH_2Cl)_8$,

$C_{40}H_{26}Cl_8N_8$ requires :

C = 53.86; H = 2.94; Cl = 30.65; N = 12.55

Found : C = 52.38; H = 3.14; Cl = 30.04; N = [8.41] Ash = 2.7 %

CHAPTER 2

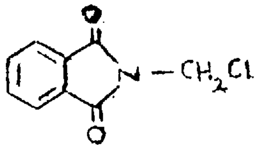
THE SYNTHESES OF 4-HALOMETHYL PHTHALONITRILES

A. Introduction

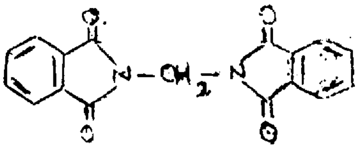
The initial purpose of this piece of work was to prepare 4-chloromethyl and perhaps 4:5 - bischloromethyl phthalonitriles, with the intention of cyclising them and their pyridinium salts to some of the compounds described in Chapter 1. However, it was realised that the synthesis in section C could be extended to give a variety of alkyl and aryl substituted phthalonitriles, and hence several new series of phthalocyanines. Consequently much of the work beyond this chapter is devoted to the preparation of alkyl substituted phthalocyanines.

B. Direct Chloromethylation of Phthalonitrile

Colaitis(29) prepared 4-methyl phthalonitrile by the rather tedious classical route of Findecklee(30) beginning with toluene. She subsequently chlorinated it to give the 4-chloromethyl derivative and cyclised this to tetrakischloromethyl phthalocyanine copper (II)(31). In view of the number of stages, and low yields involved in this route, attention was turned to the direct chloromethylation of phthalonitrile. It was appreciated that electrophilic substitution on phthalonitrile would not be easy, in view of the deactivating nature of the cyano groups, and also there was a possibility that the dinitrile system itself would be attacked. Nonetheless, Buc(32) has chloromethylated nitrobenzene and Berezovskiĭ(33) p-nitrotoluene, and it was this latter method which was tried. Phthalonitrile was mixed with $(CH_2Cl)_2O$ and chlorosulphonic acid stirred in at 50°. The mixture was left to stand overnight, and was worked up with crushed ice, yielding two products on fractional crystallisation. A lassaigne test showed that both contained nitrogen, neither contained sulphur, and the lower melting product contained chlorine. Their u.v. spectra were of the same form and typical of substituted phthalimides (see Chapter 10), and their infra-red spectra showed the typical twin carbonyls of a phthalimide at about 1770 and 1740 cm^{-1}, but lacked the N-H stretching frequencies at 3170 and 3060 cm^{-1}. These facts, together with the analyses, indicated that the two compounds had the following structures:-

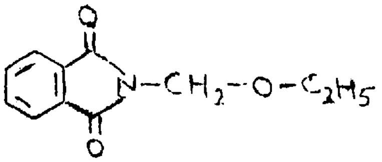


m.p. 138°



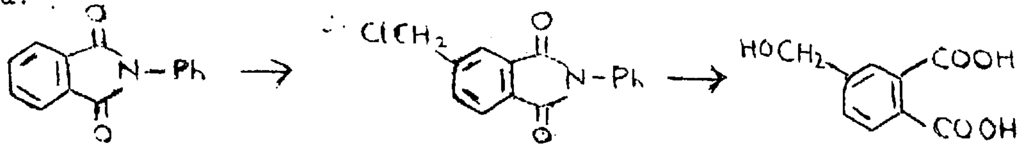
m.p. 219°

The melting point of the first agreed with a published value(34) and a mixed melting point of the second with an authentic specimen showed no depression. A second attempt to chloromethylate phthalonitrile made use of the $AlCl_3$/pyridine eutectic, and $(CH_2Cl)_2O$. Phthalonitrile was added and stirred vigorously at 85° until it had all dissolved; the product was worked up with ice, taken up in boiling ethanol and charcoaled. It was recrystallised from ethanol, and then from petroleum ether to yield once more a substituted phthalimide. The analysis and the NMR spectrum showed it to be N-ethoxy methylene-phthalimide, the methylene protons appearing as a singlet at 4.83 τ.



m.p. 84°

The melting point agreed with a published value(35), and it appears that this compound has been formed by attack of ethanol on N-chloromethyl-phthalimide. It seems likely that most chloromethylating agents will attack an o-dinitrile system to give an imide, and phthalimide itself is also more likely to be N-substituted rather than ring substituted, if used in place of the dinitrile. Randall and Renfrew(36) successfully chloromethylated N-aryl phthalimides, which can be hydrolysed to 4-hydroxymethyl phthalic acid:

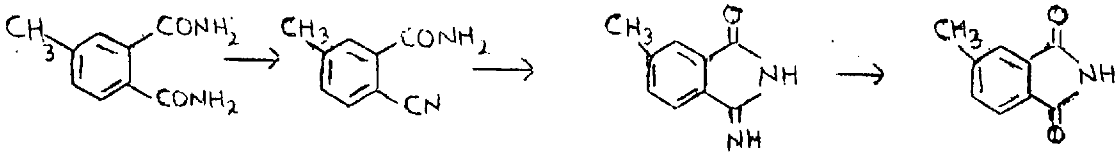


This could ultimately be converted to 4-chloromethyl-phthalonitrile, and was considered as a possible route to this compound. However it was at this stage that the potentialities of a general synthesis of phthalonitriles, using substituted dienes, were realised; and the method was tried out in the preparation of 4-methylphthalonitrile.

C. The Synthesis of 4-methyl phthalonitrile

Findecklee(30) first prepared this compound using an eight stage synthesis, starting with toluene. Many of the stages gave very low yields and involved unpleasant and messy reactions. The diene synthesis involves five stages, only one of which is unpleasant, and this gives the lowest yield of any stage namely 70%, the overall yield for the synthesis being 45-50%.

Isoprene was added to maleic anhydride in benzene solution, containing a trace of picric acid, to yield 4-methyl - 1:2:3:6 - tetrahydrophthalic anhydride(37), and this was oxidised by bromine in glacial acetic acid to 4-methyl phthalic anhydride(38). 4-methyl phthalimide was prepared by heating the anhydride slowly with 0.880 ammonia until a homogeneous melt was obtained(39), and the purified product was converted to the diamide by stirring with 0.880 ammonia for 24 hours(40). Vogel(40) recommends acetic anhydride as a dehydrating agent for phthalamide, but it was found to be insufficiently strong in this case, yielding after work up 4-methyl phthalimide:-



The best method for preparing 4-methyl phthalonitrile is to dehydrate the diamide by suspending it in hot pyridine, and passing through phosgene until the whole mass has set solid. The technique is described by Davies and Jones(41). It is essential to pass phosgene for the full time as otherwise the imide is isolated, as above. The dinitrile is readily isolated by continuous ether extraction. It shows C≡N absorption in the I.R. at 2243 cm^{-1}; compare phthalonitrile 2236 cm^{-1}.

Since both maleonitrile and fumaronitrile (cis- and trans-ethylene 1:2 - dicarbonitriles) are fairly readily available from maleic anhydride, it was thought that a Diels Alder reaction between one of these nitriles, and isoprene, followed by an aromatisation reaction, may be a more satisfactory route to 4-methyl phthalonitrile. Fumaronitrile was reacted with isoprene by refluxing in benzene, as described by Yashunskii(41), to give 1-methyl cyclohexene-trans-4:5 dinitrile. Aromatisation with bromine in glacial acetic acid yielded 4-methyl phthalimide, presumably as a result of attack on the dinitrile system by HBr. It is very likely that if dehydrogenation had been carried out by using palladium on charcoal, 4-methyl phthalonitrile would have been isolated, but as the earlier synthesis had proved so successful, it was decided not to pursue this alternative route any further.

Ultraviolet spectral data on a number of imides and dinitriles are given later (see Chapter 10) but it is appropriate at this stage to compare the spectrum as found for 4-methyl phthalonitrile, with that published by Colaïtis(29) as a number of points made in this paper, and an associated one(31) have been found to be misleading:-

Observed ('Unicam' SP500)		Colaïtis	
λ mμ	Ex10^{-3}	λ m μ	Ex10^{-3}
-	-	218	9.6
238.5(i)	10.18	-	-
243.2	10.99	240	23.2
248.3(i)	9.41	250	22.8
273.5(i)	0.83	-	-
276.0(i)	0.95	-	-
278.7	1.09	-	-
284.2	1.65	285	3.0
288.0	1.36	290	3.2
294.3	2.00	295	3.5
-	-	303	1.8

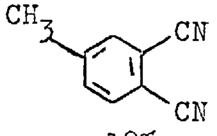
(i) denotes a point of inflection, or shoulder.

No band was observed at 303mμ, nor at 218mμ, although a very intense one ($E > 20\text{x}10^3$) occurs around 212mμ. The E values of these two sets of readings differ by a factor of two, and as the new set of figures was rechecked on a second solution, it must be concluded that the published values are incorrect.

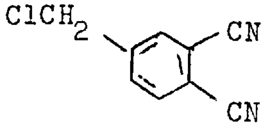
D. The halogenation of 4-methyl phthalonitrile

Bromine was found to be insufficiently reactive to bring about side-chain halogenation of 4-methyl phthalonitrile. Three attempts were made, using a mixture of bromine and calcium carbonate as a reagent, the calcium carbonate being added to remove HBr as it formed, thus preventing it from attacking the dinitrile system. In the first attempt the reagent was refluxed with the nitrile in benzene, over a 150 watt lamp; in the second it was heated with the nitrile without a solvent at 150° and in the third it was heated with the nitrile in a Carius tube at 180°. In all three cases the nitrile was recovered unchanged in good yield, accompanied in the latter case by some imide.

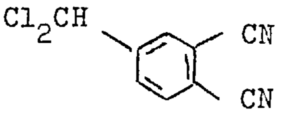
Direct chlorination, by heating the nitrile in a stream of chlorine, as described by Colaitis(29), was more successful. Careful trituration of the product with anhydrous ether, and with aqueous sodium hydroxide, gave a mixture of three compounds containing about 65% of 4-chloromethyl-phthalonitrile. The NMR. spectrum showed three bands in the aliphatic region, respectively at 7.42τ, 5.24τ and 3.08τ corresponding respectively to:-



18%



65%

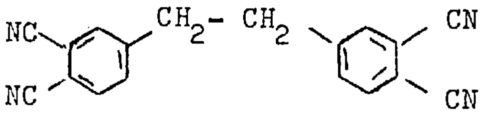


17%

Fractional sublimation failed to separate this mixture and no attempt was made to cyclise it, as described by Colaitis(31), since this would give a non-homogeneous product. However, treatment of this mixture with pyridine gave an analytical sample of <u>4-pyridinium methyl phthalonitrile chloride</u>, the methylene protons absorbing at 3.98 τ in the NMR. spectrum. It thus appears that the dichloro compound is not quaternised under these conditions. An attempt was made to cyclise the pyridinium salt to a copper pigment by heating it with urea, cuprouschloride and a trace of ammoniummolybdate in 1:2:4-trichlorobenzene, as described by Shigemitsu(43). However the mass charred, and no pigment was isolated.

It was felt that 4-bromomethyl phthalonitrile would have certain advantages over the chloro compound, since the larger bromine atom may well orientate the units during cyclisation to give a symmetrical tetrabromomethyl phthalocyanine instead of a mixture of the five predictable isomers. A search was then made for alternative methods for the side chain bromination of aromatic compounds. Bogaert-Verhoogen(44) prepared p-methoxybenzyl chloride in high yield from p-methoxy toluene, by refluxing them with 1:3-dichloro-5:5-dimethyl hydantoin in a non-polar solvent in the presence of dibenzoyl peroxide. Pickholtz and Roberts(45) record the preparation of p-nitrobenzyl bromide by refluxing p-nitro toluene in carbon tetrachloride with N-bromo succinimide, in the presence of azobis-*iso*propyl cyanide. The latter method was adapted to the bromination of 4-methyl phthalonitrile, two runs being made; one using dibenzoyl peroxide as the catalyst, the other azobis-*iso*propyl cyanide. Although the peroxide gave a better yield of bromo derivative, both runs gave a product contaminated with unchanged nitrile. Succinimide was easily removed by chromatography on alumina, but not so 4-methylphthalonitrile, so the bromide was isolated as *4-pyridinium methylphthalonitrile bromide* by quaternisation of the above mixture with pyridine. The methylene protons of this compound show a band in the

NMR spectrum at 4.02τ as compared with 3.98τ for the chloride, and the I.R. spectra of the two were identical as expected, with C≡N absorption at 2246 cm^{-1}. An attempt to cyclise the pyridinium salt to a magnesium macrocycle, using the urea melt technique, resulted once more in a charred residue. Sublimation of the salt, however, at 160°C, 10^{-4}mm gave a good yield of 4-bromomethylphthalonitrile, the methylene protons giving a band at 5.45τ and an unidentified satellite at 5.32τ in the NMR spectrum. Compare 4-chloromethyl phthalonitrile, which absorbs at 5.24τ . The I.R. spectrum of this compound shows C≡N absorption at 2241 cm^{-1} and C-Br at 665 cm^{-1}. When this bromide was fused with zinc dust at 150° , the reaction mixture suddenly set solid, but no pigment was formed. After work-up the NMR spectrum of the product was studied. The main product showed a band at 7.42τ , and hence was identified as 4-methylphthalonitrile. The I.R. spectrum confirmed this. There were also small bands at 5.45τ (starting material) and at 7.11τ which suggested that the bis-compound:



was present.

In a second run, 4-bromomethyl phthalonitrile was heated with copperbronze at 150°. After two hours, a dark blue colour was detectable presumably due to the formation of tetrakisbromomethylphthalocyanine copper(II). However, there was insufficient product to allow isolation, but the visible spectrum of the reaction mixture is recorded in chapter 10.

No further work was carried out on this topic, all future studies being devoted to alkyl substituted phthalocyanines.

E. Experimental section

N-chloromethylphthalimide and bis-N-phthalimidomethane (33A)(33B)

Phthalonitrile (5g) was stirred with $(CH_2Cl)_2O$ (10g) at 50°, and chlorsulphonic acid (11g) was slowly added over 15 min. The solution was left over night at room temperature, worked up by pouring on to crushed ice, and the semisolid mass dried in a vacuum desiccator. It was extracted on a soxhlet with light petroleum (b.p. 100-120°), a brown toffee-like material being deposited in the flask, which on recrystallisation from ethanol yielded bis-N-phthalimidomethane, m.p. 219°, undepressed when mixed with an authentic sample.

Calc. for $C_{17}H_{10}N_2O_4$:

C = 66.68, H = 3.29, N = 9.14, O = 20.89

Found : C = 66.12, H = 3.64, N = 9.04, O = 20.82 %

The hot supernatant liquor from the above soxhlet extraction deposited white crystals on cooling, and these were recrystallised from petroleum ether (b.p. 100-120°) to give N-chloromethylphthalimide, m.p. 138°. Lit(34) 136.5°.

Calc. for $C_9H_6NO_2Cl$:

C = 55.25, H = 3.09, N = 7.16 Cl = 18.32

Found : C = 55.46, H = 2.95, N = 7.51, Cl = 19.11 %

N-Ethoxymethylenephthalimide (39)

Phthalonitrile (1.5g) was added to a melt of $AlCl_3$ (9.6g) and pyridine (2.5g) containing $(CH_2Cl)_2O$ (3.3g) at 45°. The temperature was raised to 85°, and maintained there for 50 min, and the product poured on to crushed ice with violent evolution of heat. The solid residue was filtered off, taken up in boiling ethanol, charcoaled, cooled and once more crystallised from ethanol. It was then recrystallised three times from petroleum ether (b.p. 60-80°, to remove a less soluble impurity, m.p. 84°, Lit(35) 83°.

Calc. for $C_{11}H_{11}NO_3$:

C = 64.37, H = 5.40, N = 6.83, O = 23.40

Found : C = 64.71, H = 5.00, N = 7.33, O = 24.17 %

4-Methyl-1:2:3:6-tetrahydrophthalic anhydride (40), (49), (94)

Maleic anhydride (72g) was dissolved in boiling benzene (250ml) and picric acid (100 mg) added. The solution was cooled to room temperature and isoprene (50g, 74 ml) added. After an induction period, an exothermic reaction set in and the flask had to be cooled until the reaction had subsided. The flask was then heated under reflux for 20 hours, the benzene distilled off under reduced pressure and the product recrystallised from petroloum ether (b.p. 80-100°). Yield 115g, 94% m.p. 64°, Lit(37) 64-5°.

Calc. for $C_9H_{10}O_3$:

C = 65.05, H = 6.07, O = 28.88

Found : C = 65.25, H = 5.80, O = 29.13 %

4-Methylphthalic anhydride (41), (50), (95)

4-Methyltetrahydrophthalic anhydride (105g) was dissolved in glacial acetic acid (210 ml) and heated to just below its boiling point. A solution of bromine (270g) in glacial acetic acid (250ml) was added over 90 min and the mixture refluxed for 16 hours. Much HBr was evolved. The excess acetic acid was boiled off under reduced pressure, and the dark residue heated on a Wood's metal bath at 220° for nine hours, during which time more HBr was evolved. The product was recrystallised from petroleum ether (b.p. 80-100°) Yield 97g, 94% m.p. 90°, Lit(37) 88-94°.

Calc. for $C_9H_6O_3$:

C = 66.67, H = 3.72, O = 29.61

Found : C = 66.65, H = 3.89, O = 29.52 %

4-Methylphthalimide (42), (51), (97)

4-Methylphthalic anhydride (170g) was mixed to a slurry with 0.880 ammonia solution (180ml), and slowly heated on a Wood's metal bath over a period of five hours until a quiet melt was obtained (280°). The product was cooled, taken up in boiling acetone, charcoalled and evaporated to dryness. Yield 159g, 94%. A sample was recrystallised from ethanol. m.p. 196°, Lit(46) 196°.

Calc. for $C_9H_7NO_2$:

C = 67.08, H = 4.37, N = 8.69, O = 19.86

Found : C = 67.23, H = 4.37, N = 8.90, O = 20.00 %

4-Methylphthalamide (43), (53), (100).

4-Methylphthalimide (75g) was finely powdered, suspended in 0.880 ammonia solution (280ml), and stirred at room temperature for

24 hours. After about 30 min, a homogeneous brownish solution was obtained, but the product then began to precipitate yielding ultimately a semi-solid mass. This was filtered under suction, and the mother liquors were evaporated down to yield a further crop of amide. It was dried at 100°, and a sample recrystallised from ethanol. Yield 80g, 96%. m.p. 187° (decomp) Lit$^{(46)}$ 188° (decomp.).

Calc. for $C_9H_{10}N_2O_2$

C = 60.66, H = 5.65, N = 15.72, O = 17.96

Found : C = 60.24, H = 5.14, N = 15.04, O = 18.74 %

<u>4-Methylphthalonitrile</u> (48)

A. 4-Methylphthalamide (12.5g) was refluxed for 6½ hours with acetic anhydride (62ml) and the product poured into boiling water (130ml). The resulting mixture was neutralised with NaOH and rendered just acid with a few ml of dilute HCl. The aqueous suspension was submitted to a continuous ether extraction, and the product from the ether was charcoalled in ethanol and recrystallised from this solvent. It was found to be 4-methylphthalimide.

B. (54), (101)

4-Methylphthalamide (50g) was suspended in pyridine (750ml) and the mixture heated at 100° for two hours. A rapid stream of phosgene was then bubbled through the flask, so that the temperature remained around 95-100°. After 90 min the contents of the flask had set to a black tarry mass, and this was worked up with crushed ice.

The resulting black suspension was neutralised to congo red with concentrated HCl and continuously extracted with ether. The product from the ether extraction was charcoalled in ethanol, recrystallised from ethanol and then from petroleum ether (b.p.80-100°). Yield 30g, 75% m.p. 120°, Lit$^{(30)}$ 120°.

Calc. for $C_9H_6N_2$:

$C = 76.02, H = 4.26, N = 19.71$

Found : $C = 76.70, H = 4.26, N = 20.41$ %

1-Methylcyclohexene-*trans*-4:5-dinitrile (56)

Fumaronitrile (2.5g) was dissolved in benzene (10ml) and isoprene (6ml, 4.2g) added. The solution was refluxed for 20 hours and evaporated to dryness. The product was recrystallised from 100-120 petroleum ether; and then from petroleum ether (b.p. 80-100°) Two crystalline forms were isolated, and it was thought that these may be the *cis* and *trans* forms of the adduct. However, both had the same m.p. (70°) agreeing with the literature value for the *trans* material (70-70.5°)$^{(42)}$. Yield 4.0g, 85%

Calc. for $C_9H_{10}N_2$:

$C = 73.95, H = 6.90, N = 19.15$

Found : $C = 73.89, H = 6.68, N = 19.97$ %

Oxidative bromination of above (57)

1-Methylcyclohexene-*trans*-4:5-dinitrile was treated in exactly the same fashion as the tetrahydro anhydride, 3.5g of the nitrile being dissolved in acetic acid (7ml) and oxidised with a solution of bromine (9g) in acetic acid (8ml). The product had the appearance of charcoal and was finely crushed and extracted with ether. After recrystallisation from ethanol, the isolated solid was identified as 4-methylphthalimide. Yield 1.5g.

Bromination of 4-Methylphthalonitrile (58), (61), (62).

(a) 4-Methylphthalonitrile (5g) was dissolved in benzene, and calcium carbonate (2g) and water (0.5ml) added. The mixture was brought to the boil and a solution of bromine (5.5g) in benzene (15ml) added over 30 min, and the whole refluxed on a steam bath for 60 min. The bath was then replaced by a 150 watt lamp, the mixture being stirred vigorously for a further 180 min. The product was stirred with zinc dust to remove excess bromine, filtered, charcoalled and evaporated to dryness. The residue was identified as unchanged starting material.

(b) 4-Methylphthalonitrile was heated to 150° on a Wood's metal bath, and calcium carbonate (2g) added. The slurry was stirred vigorously and bromine (5.5g) added dropwise over 20 min. The mixture was heated with stirring for a further 60 min, cooled, and zinc dust added, and the whole filtered. The solution was evaporated down, excess ether added to precipitate $ZnBr_2$ and $CaBr_2$, and the filtered solution evaporated to dryness. The product was identified as the unchanged nitrile.

(c) 4-Methylphthalonitrile, (5g) calcium carbonate (2g) and bromine (5.5g) were sealed together in a carius tube and heated at

180° for 14 hours. The tube was cooled in liquid nitrogen before unsealing, in order to condense CO_2, and it was found that all the bromine had reacted. The brown, hygroscopic residue was extracted on a soxhlet with ether, and yielded unchanged dinitrile and some 4-methylphthalimide.

Chlorination of 4-methylphthalonitrile (73)

4-Methylphthalonitrile (5g) was heated to 150° on a Wood's metal bath, and a slow stream of chlorine passed over the surface of the melt for 100 min, the temperature being allowed to rise slowly to 170°. Colaïtis(29) recommends a temperature of 180°, but it was found that these conditions caused the nitrile to sublime out of the reaction vessel. The product was taken up in anhydrous ether, filtered, evaporated to dryness, triturated with two portions of N NaOH to remove imide, washed with dilute HCl and with water. It was recrystallised from acetone after charcoalling in that solvent. The product was obviously still a mixture from the I.R. spectrum.

m.p. 53-4° (fine needles left in suspension) Lit(29) 28-30°.

Calc. for $C_9H_5N_2Cl$:

C = 61.20, H = 2.85, N = 15.86, Cl = 20.08

Found : C = 57.38, H = 3.30, N = 15.12, Cl = 21.97 %

4-Pyridinummethylphthalonitrile chloride (83)

4-Chloromethylphthalonitrile (impure, 690 mg) was dissolved in pyridine (5ml) and the mixture refluxed for 2 min. The product was left to stand for 30 min. and the small white crystals filtered off. They were taken up in hot ethanol, filtered through charcoal and the solution allowed to crystallise. Yield 590 mg, 90% on a basis of 65% starting material.

$C_{14}H_{10}N_3Cl$ requires :
C = 65.76, H = 3.94, N = 16.44, Cl = 13.88
Found : C = 66.22, H = 3.97, N = 16.29, Cl = 13.54 %

Attempted cyclisation of the pyridinium salt (87)

The pyridinium salt (200mg) was finely ground with urea (1.0g), cuprous chloride (20mg) and ammonium molybdate (10mg). This mixture was stirred with 1:2:4 trichlorobenzene (10ml), slowly heated over 60 min to 170°, and maintained at this temperature for 180 min. The product appeared as a black charred suspension in the trichlorobenzene, and no pigment was isolated.

4-Pyridinium methylphthalonitrilebromide (111), (116)

Two preparation were carried out under very similar conditions, the first making use of dibenzoyl peroxide as a catalyst, and the second, described here, azobisisopropylcyanide. 4-Methylphthalonitrile (5g) was dissolved in boiling carbon tetrachloride (100ml), and N-bromosuccinimide (6.5g) added, immediately followed by 50mg azobis<u>iso</u>propylcyanide. Refluxing was continued for 80 hours, a second addition of the catalyst (50mg) being made after 24 hours. The solvent was evaporated off and the product ground with anhydrous ether (30ml), the insoluble succinimide being filtered off. After dilution with acetone (150ml) the boiling solution was charcoaled, evaporated to dryness, taken up in benzene (25ml), filtered, and run on to the top of an alumina column (23 x 1.5cm). The column was developed with benzene, 250ml being required to elute the product, now freed from carbonyl compounds. It still contained unchanged starting material, so was dissolved in pyridine, and the precipitated salt collected after standing at room temperature for 16 hours. It was recrystallised from ethanol/water (10:1). Yield 1.83g, 18%. Dibenzoyl peroxide as a catalyst gave 34% yield.

$C_{14}H_{10}N_3Br$ requires:

C = 56.03, H = 3.36, N = 14.00, Br = 26.61

Found : C = 55.85, H = 4.13, N = 14.10, Br = 26.57 %

Attempted cyclisation of pyridinium salt (128)

4-Pyridiniummethylphthalonitrilebromide (0.5g) was mixed with urea (15g) and magnesium turnings (0.1g) and a little boric acid (0.1g) added. The mixture was heated to 180° and the temperature held there for 120 min. No pigment was isolated.

4-Bromomethylphthalonitrile (111B)

A sample of the pyridinium salt was heated at 160°, 10^{-4}mm pressure, and a low melting solid was observed to condense on the walls of the sublimation apparatus. It was recrystallised from acetone. m.p. 74-5°.

$C_9H_5N_2Br$ requires:

C = 48.88, H = 2.28, N = 12,68, Br = 36.16

Found : C = 49.55, H = 2.29, N = 12.98, Br = 36.88 %

Reduction with zinc dust (117)

4-Bromomethylphthalonitrile (1.0g) was heated with zinc dust (0.3g) on a Wood's metal bath at 160°. After a while the mass solidified, but there was no evidence of pigment formation. The product was extracted on a soxhlet with acetone, the brown solution filtered through charcoal and evaporated to dryness. The product was identified from its N.M.R. spectrum in $CDCl_3$ as 4-methylphthalonitrile, with a little starting material and also bis-4-methylenephthalonitrile.

CHAPTER 3

TETRAKIS-4-METHYLPHTHALOCYANINES

A. Introduction

Tetrakis-4-methylphthalocyanine copper (II) seems to be the only compound in this series to have been recorded to date in the literature(31)(47) and here the information available is very limited, and to a certain extent inaccurate(31). In this section, several methods of preparation are given for the metal free pigment, and the derivatives of seven metals are described, namely those of sodium, magnesium, iron, cobalt, copper, zinc and tin.

B. Tetrakis-4-methylphthalocyanine

When phthalonitrile is heated with a methanolic solution of ammonia, 1 : 3-di-imino-*iso*indoline is formed(48). This can be cyclised to phthalocyanine in boiling tetralin as described by Elvidge and Linstead(49). 4-Methylphthalonitrile was heated in a Carius tube with methanol and liquid ammonia, to give a red solution. This was charcoalled and recrystallised to give 5-methyl-1 : 3-di-imino*iso*indoline contaminated with some dinitrile and imide. Attempts to purify it were unsuccessful. However, a few blue crystals were isolated from the Carius tube, and although there was insufficient for analysis, the visible spectrum in 1-chloronaphthalene was of the same form as that of phthalocyanine(50), but with the peaks shifted to longer wavelengths. Later work confirmed that this was tetrakis-4-methylphthalocyanine. A sample of the crude di-imino*iso*indoline was refluxed in boiling tetralin, but although ammonia was evolved, no pigment was isolated. The conditions for preparing a di-imino*iso*indoline from a particular dinitrile are very critical(42), and rather than use up a quantity of 4-methylphthalonitrile in finding the best conditions here, attention was turned to alternative methods of preparing the metal-free pigment.

Phthalocyanine itself was first prepared by the action of acids on the magnesium pigment(4), so this technique was investigated. 4-Methylphthalonitrile was fused with magnesium turnings until the mass had solidified. The product after grinding with ethanol was dissolved in concentrated sulphuric acid, filtered through glass wool, poured into cold water and left to stand over night. The fine blue precipitate was washed and recrystallised to give two products, one a mixture of tetrakis-4-methylphthalocyanine and the magnesium derivative, and the other practically pure *tetrakis-4-methylphthalocyanine aquomagnesium*. It thus appears that the tetrakismethyl magnesium pigment is more difficult to demetallate than is phthalocyanine magnesium; and this was confirmed later when studies were made on the disodium derivative.

Geigy(51) describes the preparation of phthalocyanine by refluxing a mixture of 69% aqueous sodium sulphide and phthalonitrile in 2-methoxyethanol. Several runs were made using phthalonitrile in place of the 4-methyl derivative, in order to find the optimum conditions. The best yield obtained was 58%, and it was noted that the quantity of sodium sulphide and the heating time was very critical. Several of the runs are listed in Table II, most of which were carried out under conditions different from those recommended by Geigy. Unless otherwise stated 1g of phthalonitrile was used in 25 ml 2-ethoxyethanol, the quantity of anhydrous Na_2S being varied.

Table II

Na_2S/nitrile Mol.ratio	Temp. (°C)	Heating time	Yield pigment	Comments
1 : 1	100	2hrs then left at room temperature 18 hrs	0.5%	Crimson coloured supernatant liquid, white solid deposited.
1 : 2	100	2hrs then left at room temperature 18 hrs	0.2%	As above but only about half as much white solid. $Na_2S.9H_2O$ used.
1 : 2	100	2hrs then left at room temperature 18 hrs	12 %	Brownish yellow supernatant liquid.
1 : 3	100	2 hrs then left at room temperature 18 hrs	20%	Brownish green supernatant liquid.
1 : 4	50	48 hours	50%	Dark yellow supernatant liquid.
1 : 6	100	1 hour	35%	" "
1 : 6	100	3½ hours	53%	" "
1 : 6	100	3½ hours	58%	" "
1 : 6	100	21 hours	39%	" "
1 : 10	100	5 hours	25%	" "
1 : 10	100	21 hours	20%	" "
1 : 20	130	3 hours	16%	2.56g nitrile, 3.6g 2-methoxy ethanol, $Na_2S.9H_2O$ Brownish yellow supernatant liquid

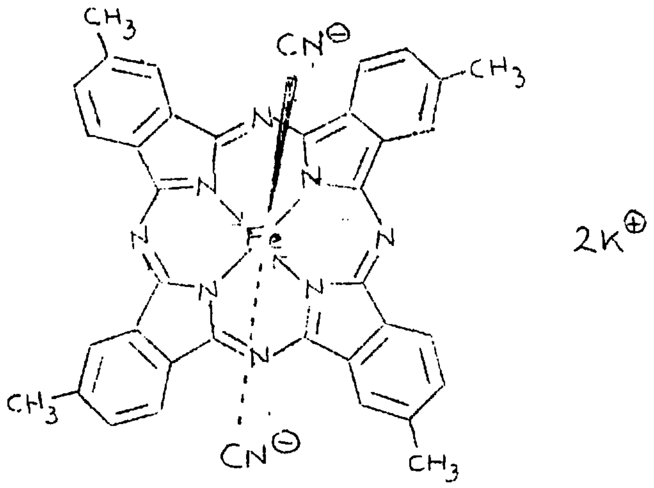
The crimson solution observed in the first two runs gave a yellowish brown precipitate on being poured into water, and a mauve solution in acetone.

When this technique was applied to 4-methylphthalonitrile, no pigment was isolated, and although it was felt that there was room for more work here, this method was abandoned in favour of the following one.

Linstead and Lowe(5) prepared phthalocyanine by hydrolysis of the disodium salt, and this technique was applied to the 4-methyl derivative with great success. 4-methylphthalonitrile was added to a boiling solution of sodium in n-amylalcohol to give <u>tetrakis-4-methylphthalocyanine disodium</u>. This was purified and then refluxed for two days with 4N hydrochloric acid. O-Dichlorobenzene extraction deposited bright coppery needles of <u>tetrakis-4-methylphthalocyanine</u>, analytically pure. It was found to be appreciably more soluble than phthalocyanine, and samples were recrystallised from chlorobenzene, diphenyl ether and pyridine. The visible spectrum was identical with that of the compound isolated in the Carius tube reaction, and is recorded in Chapter 10. The great stability of the disodium derivative is illustrated by the necessity to reflux it for two days with strong acid before the metal is removed. This stability is even more enhanced in the case of the octakismethyl and tetrakis-3-methyl disodium derivatives described later, and is a little difficult to explain. It is possible that the positive inductive effects due to the methyl groups result in a greater electron density at the centre of the phthalocyanine ring, hence giving the Na ---N bond more covalent character. This would render the sodium less labile.

C. Tetrakis-4-methylphthalocyanine iron (II)

The primary purpose of this piece of work was to prepare if possible, a complex between the title compound and potassium cyanide. Lever(52) had prepared a similar complex with phthalocyanine iron (II) in this department, and had found it to be very soluble in methanolic potassium cyanide, besides being diamagnetic. These properties make an N.M.R. study on the compound a distinct possibility. The following work was carried out at the end of the research programme, when the supply of 4-methylphthalonitrile was very low. Consequently, in view of the small quantities involved, emphasis was laid on obtaining sufficient cyanide complex (about 50 mg required for N.M.R. study) rather than isolating intermediates analytically pure. Tetrakis-4-methylphthalocyanine iron (II) was prepared by heating together ferric acetate and 4-methylphthalonitrile. It was recrystallised from chlorobenzene and then from pyridine, in which it was very soluble, and finally dried at 200° in vacuo to remove any solvated molecules. An analysis showed it to be impure. An intense green solution was obtained when it was refluxed with methanolic potassium-cyanide and after filtration and evaporation to dryness, a green powder was isolated, being very soluble in methanol, and soluble in ethanol and in water, though it was slowly hydrolysed by this latter. It was identified as dipotassium [tetrakis-4-methylphthalocyanine dicyanoferrate (II)], since sharp bands in the N.M.R. spectrum showed it to be diamagnetic. The N.M.R. spectrum in methanolic potassium-cyanide will be discussed in full in Chapter 8, but it is worth noting here that it was of the form which would be expected from a 4-substituted phenylene ring, fused to a second aromatic system, confirming the structure as :



There was no fine splitting in the bands, which was interpreted as meaning either that the five possible isomers were indistinguishable at 60 Mc, or that only one isomer was present (presumably the symmetrical form shown above).

D. Tetrakis-4-methylphthalocyanine cobalt (II)

When the metal free pigment was extracted into a suspension of anhydrous cobalt chloride in o-dichlorobenzene, there was no appreciable formation of the cobalt derivative. Substitution of the chloride by cobalt acetate, however, gave beautiful coppery needles, which dissolved in boiling o-dichlorobenzene to give a bright blue solution. Although the crystals were homogeneous under the microscope, and unchanged by repeated recrystallisations, they none the less analysed as a 50 : 50 mixture of the cobalt and metal free pigments. That the material was truly a mixture was confirmed by the observation of broad peaks in the visible and infra-red spectrum, corresponding to the superimposition of the true bands, and also by chromatography on alumina. Two bands separated, one bluish green and the other deep blue. It appears that a 50 : 50 mixture crystallises in a stable lattice, since three recrystallisations from o-dichlorobenzene failed to change the composition. A similar effect was observed by Ficken(53) during a preparation of nickel tetracyclohexeno tetrazaporphyrin from the metal free pigment and nickel chloride in chlorobenzene. He obtained a stable 70 : 30 mixture, finding that the metal free pigment deposited on to crystals of the nickel compound as they formed. This was also observed during the preparation of the palladium pigment. The problem may be overcome by using a higher boiling solvent in which the mixed crystals are more soluble, hence allowing reaction with the metal salt to go to completion. However, <u>tetrakis-4-methylphthalocyanine cobalt (II)</u> was successfully prepared by heating together 4-methylphthalonitrile and cobalt acetate. It crystallised in fine reddish needles from o-dichlorobenzene, being quite soluble in that solvent, giving a rich royal blue solution. It was also readily soluble in boiling pyridine, presumably forming a monopyridinate.

E. Tetrakis-4-methylphthalocyanine Copper (II)

Colaïtis(31) prepared this derivative by heating together 4-methylphthalonitrile and copper bronze. She records that it is insoluble in the usual organic solvent, is non-crystalline and lacks a metallic lustre.

This preparation was repeated using anhydrous copper sulphate in place of copper bronze, and a good yield of pigment was obtained. It was re-crystallised from o-dichlorobenzene to give blue needle-like crystals with a coppery reflex. Crystals were obtained only after the third recrystallisation so it is possible that Colaitis's sample was insufficiently purified; the only analytical data she recorded being in the form of carbon to nitrogen atomic ratios. The copper derivative was also prepared in excellent yield by extracting the metal free pigment into a suspension of cupric acetate in o-dichlorobenzene. This sample was spectroscopically identical with the one prepared from the nitrile and copper sulphate. Although this compound is more soluble than copperphthalocyanine, being sufficiently soluble in chlorobenzene to be recrystallised from that solvent, it does not dissolve as readily as the cobalt derivative, and is insoluble in pyridine.

F. Tetrakis-4-methylphthalocyanine zinc

When zinc dust was ground with 4-methylphthalonitrile and the mixture fused at about 250°, tetrakis-4-methylphthalocyanine aquozinc was isolated as small blue crystals after recrystallisation from chlorobenzene. This monohydrate is very stable, retaining its one molecule of water even after being heated for two hours at 150°, 0.02 mm. Phthalocyanine zinc forms a similar monohydrate, stable to heat(27). The pigment is much more soluble than even the cobalt derivative, and may be recrystallised from benzene, in which it gives a bluish green solution. Recrystallisation from pyridine, in which it is extremely soluble, yields <u>tetrakis-4-methylphthalocyanine pyridine zinc</u> as dark blue crystals. In these respects the tetrakis-4-methyl derivative behaves in much the same way as phthalocyanine zinc but is more soluble.

G. <u>Derivatives of tin (IV)</u>

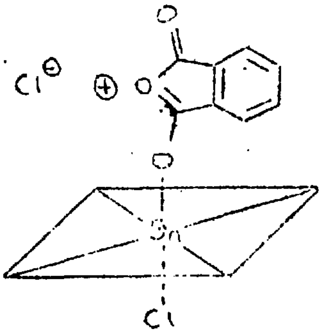
Barrett, Dent and Linstead(27) found that when anhydrous stannous chloride and phthalonitrile were heated together, a strongly exothermic reaction took place, accompanied by a change in the valence state of the tin to yield phthalocyanine dichlorotin(IV). When this reaction was repeated, using 4-methylphthalonitrile, a good yield of tetrakis-4-methylphthalocyanine dichlorotin (IV) was obtained. It was recrystallised from chlorobenzene, in which it was quite appreciably soluble, to give bluish green prisms, with a faint bluish metallic sheen. In solution it was bright green.

In an earlier attempt to prepare this compound, hydrated stannous chloride was mistakenly used in place of the anhydrous material, and when heating was commenced, there was considerable evolution of water. This was followed by a violent exothermal reaction in which the temperature in the flask rose 50° above that of the heating bath, which was maintained at 240°. The product was recrystallised repeatedly from chlorobenzene, between each recrystallisation being ground and extracted with ethanol and acetone (this was the usual procedure adopted throughout this work in the purification of phthalocyanines, though naturally the recrystallising solvent was not always chlorobenzene).

A bright green powder was isolated, being made up of rough translucent crystals, which were very brittle and easily crushed. Complete analysis showed that the material was made up of a 1 : 1 mixture of tetrakis-4-methylphthalocyanine dichlorotin(IV) and $C_9H_6O_3$ - a 4-methylphthalic anhydride residue, formed by hydrolysis of the dinitrile. It was at first thought that it was a genuine mixture of the two compounds. However, the visible spectrum was shown to be quite appreciably different from that of authentic tetrakis-4-methylphthalocyanine dichlorotin(IV), the bands being generally increased in intensity, and shifted to lower wavelengths :

$(4\text{-Me})_4SnCl_2Pc$	λ (Å) :	3675	5980	6150	6410	6830	7130
	$\log_{10} \varepsilon$:	4.74	3.51	3.75	4.47	4.40	5.22
Anhydride	λ (Å) :	3690	5840	6130	6342	6780	7045
Complex	$\log_{10} \varepsilon$:	4.79	3.71	3.89	4.52	4.46	5.26

The I.R. spectrum of the anhydride complex, though showing additional weak absorption at 1768, 1720, 1680, 1497 and 747 cm^{-1} lacked the strong carbonyl absorptions at 1858 and 1776 cm^{-1}, the C - O - C stretching mode at 1264 cm^{-1}, and the strong band at 895 cm^{-1}, characteristic of phthalic anhydrides. Finally, a preliminary X-ray study, carried out by Dr. Rogers of this department, showed that the compound was non-crystalline, and probably polymeric. This latter observation, though explaining admirably the brittle nature of the 'crystals' poses the biggest problem of all regarding the structure of this complex. Elvidge and Lever(54) observed that six co-ordinate chromium complexes with acetate residues attached to the chromium atom show weak absorption at 1714±5cm^{-1}, and at 1489±5cm^{-1}, the latter being found in all six coordinate complexes. It must however be noted that both of the compounds under discussion show a band at 1487cm^{-1}. Apparently the anhydride residue has been modified in some way, whilst the tin atom still remains six coordinate. Forgetting for the time being the polymeric nature of the complex, two structures can be postulated, and between them they may throw light on the true structure.



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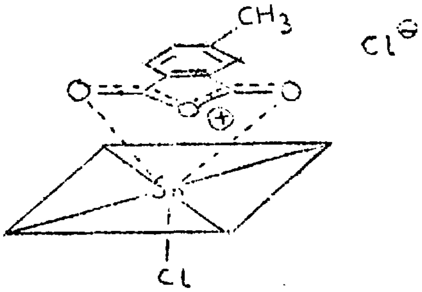
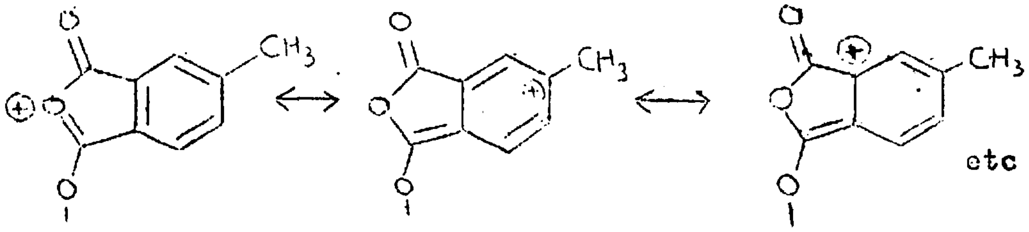
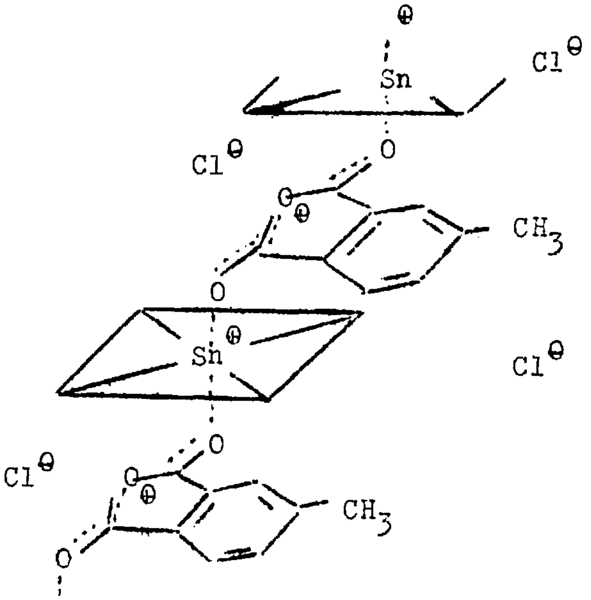


II

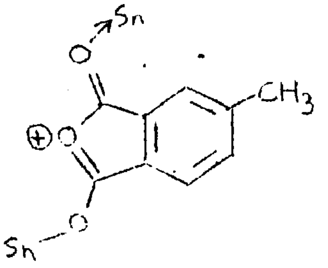
Structure I is an oxonium salt, the plane of the anhydride lying at about 120° to the plane of the phthalocyanine ring the positive charge being stabilised as follows:

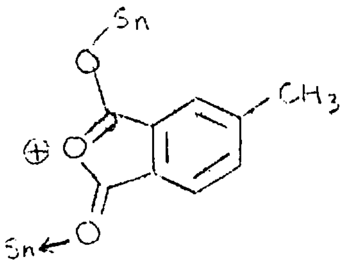


Structure II results from overlap of an empty 5d or 4f orbital of the tin atom with the π electron system of the 5-ring anhydride, the positive charge being more evenly distributed and the plane of the anhydride being parallel to the plane of the phthalocyanine. Combining these two models and bearing in mind the polymene nature of the product, we can draw a structure which should be reasonably stable:

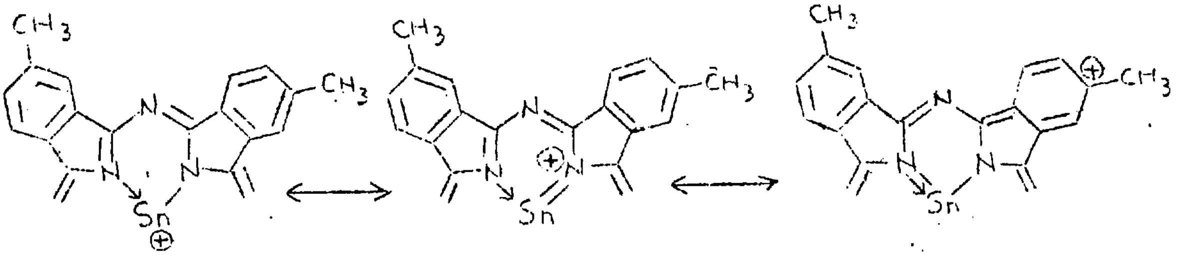


The anhydride would be stabilised as before, with additional contributions from the two resonating forms:





The positive charge on the tin atom could be stabilised by conjugation to the aromatic phthalocyanine system:



The chloride ions could fit into the lattice as shown above, so as to be as close as possible to the positive charges. The structure postulated above, though unsatisfactory in some respects, does explain the data available on this compound, including the hypsochromic shift of the bands in the visible spectrum, accompanied by an increase in E_{max}. There is room for further detailed study here.

H. Summary of the properties of Tetrakis-4-methylphthalocyanines

These pigments are in general prepared as easily as the parent unsubstituted phthalocyanines, and in appearance are of much the same crystalline form, having a characteristic metallic lustre. They are, however, more soluble in aromatic solvents, though still in the order of a few mg per 100ml of solvent, giving blue to green solutions. The visible spectra (see chapter 10) are of the same form as the parent compounds but the principal absorption maximum around 7000Å is shifted by about 100Å to longer wavelengths. In the infrared there are some marked differences, these being discussed in chapter 9, but members of the series show bands in common.

The enhanced solubility may be attributed to three factors.

(i) The methyl groups will tend to push molecules further apart in the lattice and hence lower the lattice energy.

(ii) The methyl groups provide points of 'attraction' to solvent molecules.

(iii) Each member of this series, instead of being a pure compound will be made up of anything up to all five of the possible isomers.

From the evidence of the disodium and magnesium derivatives, it appears that the metal is more firmly bonded than in the parent compounds.

J. Experimental section

5-Methyl-1:3-diiminoisoindoline (63)

4-Methylphthalonitrile (5g) was placed in a carius tube, and to this was added a solution of liquid ammonia (10ml) in methanol (30ml). The tube was heated at 100° for 4½ hours. Filtration of the red brown solution yielded a few mg of tetrakis-4-methylphthalocyanine. The filtrate was evaporated to dryness, taken up in boiling methanol filtered twice through charcoal, and crystallised from methanol/ether. The product was impure.

Cyclisation in tetralin (64)

Impure 5-methyl-1:3-diiminoisoindoline (0.33g) was refluxed in boiling **tetralin** for 60 min (207°). Ammonia was evolved, but no pigment isolated.

Tetrakis-4-methylphthalocyanine magnesium (65)

4-Methylphthalonitrile (5g) was heated with magnesium turnings (0.3g) at 250°, with stirring, until the mass had set solid. After cooling, this was finely ground, extracted with ethanol to remove unchanged nitrile, and degradation products, and dissolved with stirring in concentrated sulphuric acid (25ml). This solution was filtered through glass wool, and slowly poured into five times its volume of water, the hot blue suspension being left to stand for 18 hours. The precipitate was filtered off, washed well with water, dried and extracted with ether until the extracts were colourless. It was then extracted with benzene to yield product A, and the residue recrystallised from chlorobenzene to give product B.

Product A. $C_{36}H_{26}N_8$ requires :

C = 75.76, H = 4.59, N = 19.65

Found : C = 72.63, H = 4.42, N = $\left[16.15\right]$ % ash = ~1%

Product B. $C_{36}H_{26}MgN_8O$ requires :

C = 70.78, H = 4.29, Mg = 3.98, N = 18.33

Found : C = 71.32, H = 4.35, Mg = 2.27, N = $\left[14.56\right]$ %

Phthalocyanine (84), (86)

A typical run is described. Phthalonitrile (1.0g) was dissolved in 2-ethoxyethanol (25ml) in a boiling tube, and finely divided anhydrous sodium sulphide (0.20g) was added. The tube was plugged with cotton wool, heated on a steam bath for 2 hours and then left to stand at room temperature overnight. The brownish green solution was filtered and the deposited solid washed well with acetone and ethanol, and dried. Yield 0.20g, 20%. In this run the ratio of Na_2S/Nitrile was 1:3 molar.

Run using 4-methylphthalonitrile (107)

4-Methylphthalonitrile (5g) was heated with 2-methoxy-ethanol (6.35g) and 69% sodium sulphide solution (0.6g) added. The solution was boiled for 3 hours, but no pigment was isolated due to an excessive quantity of sodium sulphide being present.

Tetrakis-4-methylphthalocyanine disodium (108)

Sodium (0.9g) was dissolved in n-amyl alcohol (50ml) and the solution brought to the boil. 4-Methylphthalonitrile (5g) was added and boiling continued for 10 min. The product was cooled, diluted with acetone, filtered, finely ground and extracted with ethanol and then acetone. Yield 1.6g, 28%

Tetrakis-4-methylphthalocyanine (108)

The disodium derivative (1.6g) was refluxed for 24 hours with ethanol/HCl, after which it was found still to contain metal. It was finely ground and refluxed with 4N HCl for a further 24 hours, to yield after one crystallisation from chlorobenzene, 975mg, 67%. It was recrystallised twice more from chlorobenzene, and then once from o-dichlorobenzene, to give bright coppery needles.

$C_{36}H_{26}N_8$ requires :

C = 75.76, H = 4.59, N = 19.65

Found : C = 75.93, H = 4.61, N = 19.87 %

Tetrakis-4-methylphthalocyanine iron(II)

4-Methylphthalonitrile (0.7g) was finely ground with ferric acetate (0.2g) and the mixture heated at 280° for 30 min (Wood's metal bath). The product was powdered, extracted overnight with acetone, recrystallised three times from chlorobenzene, and then once from pyridine. It was dried at 200°, 10mm to remove pyridine. Yield 100mg.

$C_{36}H_{24}FeN_8$ requires :

C = 69.25, H = 3.87, N = 17.94

Found : C = 64.10, H = 3.50, N = 15.61 %

Dipotassium [tetrakis-4-methylphthalocyanine dicyanoferrate (II)]

Tetrakis-4-methylphthalocyanine iron (II) (100mg) was added to a solution of potassium cyanide (50mg) in ethanol (5ml), and the mixture refluxed for 48 hours. It was diluted with methanol (10ml) filtered, and evaporated under reduced pressure. The product was taken up in methanol (10ml) containing a little KCN, refiltered and once more evaporated under reduced pressure. The resulting solid was taken up in the minimum quantity of methanol ($\sim$0.8ml) in which it was very soluble and the N.M.R. spectrum studied.

Tetrakis-4-methylphthalocyanine cobalt(II) (113), (115),

(a) Anhydrous $CoCl_2$ (50mg) was suspended in o-dichlorobenzene (10ml) and tetrakis-4-methyl-phthalocyanine (130mg) extracted into the boiling suspension. No metallated pigment was isolated.

(b) The above was repeated, using $Co(OAc)_2$ hydrate in place of the chloride. The cooled product was filtered, washed with water, dilute acetic acid (200ml), ethanol and then acetone. It was recrystallised three times from o-dichlorobenzene.

$C_{36}H_{24}N_8Co + C_{36}H_{26}N_8$ requires :

C = 71.78, H = 4.18, Co = 5.43, N = 18.61

Found : C = 71.85, H = 4.44, Co = 5.04, N = 18.94 %

(c) 4-Methylphthalonitrile (2.0g) was mixed with anhydrous $Co(OAc)_2$ (0.8g) and then heated at 220-265°C on a Wood's metal bath. The reaction was strongly exothermal. The product was worked up in the usual fashion, and recrystallised three times from o-dichlorobenzene.

$C_{36}H_{24}CoN_8$ requires :

C = 68.93, H = 3.85, N = 17.83

Found : C = 68.79, H = 4.21, N = 17.81 %

Tetrakis-4-methylphthalocyanine copper (II) (112), (158)

(a) Tetrakis-4-methylphthalocyanine (70mg) was suspended in boiling o-dichlorobenzene, and an excess of finely powdered $Cu(OAc)_2$ hydrate added. The mixture was boiled for 10 min, cooled, filtered, and the product washed well with acetone, water and ethanol, It was three times recrystallised from o-dichlorobenzene. Yield 60mg, 78%

Calc. for $C_{36}H_{24}CuN_8$

C = 68.42, H = 3.82, Cu = 10.04, N = 17.72

Found : C = 68.37, H = 4.56, Cu = 9.54, N = 17.84 %

(b) 4-Methylphthalonitrile (1.0g) was finely ground with anhydrous $CuSO_4$ (0.3g) and the mixture heated on a Wood's metal bath at 230°. The product was worked up in the usual fashion and recrystallised twice from chlorobenzene. Yield 200mg, 18%

Tetrakis-4-methylphthalocyanine aquozinc (59)

4-Methylphthalonitrile (5g) was heated with zinc dust (0.65g), the melt becoming green at 210°, pasty at 250° and finally solid after heating at this temperature for 20 min. The product was worked up in the usual fashion, the analytical sample being recrystallised from chlorobenzene, though it was sufficiently soluble in boiling benzene.

$C_{36}H_{26}N_8OZn$, requires :

C = 66.30, H = 4.02, N = 17.18, Zn = 10.02

Found : C = 66.09, H = 4.21, N = 17.38, Zn = 7.39 (in ash) %

Tetrakis-4-methylphthalocyanine pyridine zinc (89)

A sample of the monohydrate above was twice recrystallised from boiling pyridine and dried at 100°/15mm.

$C_{41}H_{29}N_9Zn$ requires :

C = 69.05, H = 4.10, N = 17.69

Found : C = 69.24, H = 3.95, N = 17.74 %

Tetrakis-4-methylphthalocyanine dichlorotin (IV) (92), (106)

Stannous chloride (1.0g, dried in air for 2 hours at 170°) was mixed with 4-methylphthalonitrile (3.0g), and the mixture heated on a Wood's metal bath maintained at 220°. The temperature of the melt rose to 250°C, and the product was worked up in the usual fashion.

It was recrystallised four times from chlorobenzene, being reground and extracted with acetone between each recrystallisation. The run was repeated on three times the scale, this time the temperature of the melt rising to 315°.

$C_{36}H_{24}Cl_2N_8Sn$ requires :

C = 57.02, H = 3.19, Cl = 9.35, N = 14.79

Found : C = 5~~7~~6.96, H = 3.35, Cl = 9.66, N = 14.41

Found : C = 56.98, H = 3.49, Cl = 9.74, N = 15.04 %

Anhydride complex (78)

4-Methylphthalonitrile (3g) was mixed with hydrated stannous chloride (2.0g) and heated on a Wood's metal bath maintained at 220°. Melting, and evolution of steam took place, ceasing when the melt had reached 170°. The temperature of the melt continued to climb, and at 240° a violent exothermal reaction took place, the temperature of the mixture rising to 290°. The product was worked up in the usual way and recrystallised exactly as described for the authentic tetrakis-4-methylphthalocyanine dichlorotin (IV) above.

$C_{45}H_{30}N_8Cl_2O_3Sn$ requires :

C = 58.69, H = 3.28, Cl = 7.71, N = 12.18, O = 5.22, Sn = 12.90

Found : C = 58.75, H = 3.60, Cl = 7.35, N = 12.19, O = 6.22, Sn = 12.25 %

(on SnO_2)

CHAPTER 4

THE TETRAKIS-4:5-DIMETHYLPHTHALOCYANINES

A. Introduction

It was shown in the last chapter that the tetrakis-4-methyl phthalocyanines are more soluble than their parent analogs, so it seemed logical to investigate whether the addition of four more methyl groups would enhance the solubility even further, or decrease it in view of the symmetry of the resulting structure. There were also advantages to be gained from a study of the infra red spectra of these compounds alongside those of the tetrakis-4-methyl series, as such studies might help in the assignment of bands observed in the unsubstituted phthalocyanines.

The copper derivative was first prepared by de Diesbach and Von der Weid(2), and later by Colaïtis(31), but these seem to be the only references to this series. In this work the diene synthesis was used.

B. The synthesis of 4:5-dimethylphthalonitrile

The synthesis was carried out in a fashion analogous to the preparation of 4-methylphthalonitrile, only using 2:3-dimethyl-1:3-butadiene in place of isoprene.

Pinacol hydrate was prepared by the method of Adams(55) by the reduction of acetone with magnesium amalgam. It was dehydrated to anhydrous pinacol by distilling with benzene, and then gently refluxed with 45% hydrobromic acid to give 2:3-dimethyl butadiene(56). Reaction with maleic anhydride in benzene, in the presence of picric acid gave 4:5-dimethyl-1:2:3:6-tetrahydrophthalic anhydride, and this was oxidised by bromine in glacial acetic acid to give 4:5-dimethylphthalic anhydride. When heated slowly to 280° with 0·880 ammonia solution, the anhydride was converted to 4:5-dimethylphthalimide and this on stirring for 24 hours with 0.880 ammonia gave a good yield of 4:5-dimethylphthalamide. Dehydration of the amide by phosgene in pyridine solution produced 4:5-dimethyl-phthalonitrile, with the C≡N absorbing in the infra red at 2239cm^{-1}, and the spectrum having an interesting triplet made up of three bands respectively at 1297, 1279 and 1261cm^{-1}. This is a useful feature for identifying this compound. The structure of 4:5-dimethylphthalic anhydride was confirmed by an N.M.R. study, the methyl groups absorbing at 7.50τ and the two aromatic protons at 2.22τ. Since the aromatisation stage was the one in which a rearrangement was most likely to occur, it was justifiably assumed that the structure of the dinitrile was the correct one.

C. Tetrakis-4:5-dimethylphthalocyanines

(i) Tetrakis-4:5-dimethylphthalocyanine

During the studies made into the preparation of phthalocyanine from the phthalonitrile, using Geigy's method(51), the best yield was obtained by using a 1:6 molecular ratio of sodium sulphide to the nitrile and heating at 100° in 2-ethoxy-ethanol for $3\frac{1}{2}$ hours. These conditions were repeated, using 4:5-dimethylphthalonitrile, but no pigment was isolated. It seems that although the conditions of this reaction are very critical, they vary with the nitrile used.

The preparation was repeated using 2-methoxy-ethanol and aqueous sodium sulphide, refluxing these with the dinitrile as recommended in the original patent(51). This time some pigment was isolated in very low yield, and although it was worked up under the recommended hydrolysing conditions with dilute sodium hydroxide solution, the product was shown to contain about 4% of sodium.

(ii) Tetrakis-4:5-dimethylphthalocyanine disodium

When 4:5-dimethylphthalonitrile was refluxed with a solution of sodium amyloxide in n-amyl alcohol a 25% yield of Tetrakis-4:5-dimethylphthalocyanine disodium was formed. It was necessary to reflux this material with acid for three days in order to remove the sodium, and recrystallisation of the product from boiling 1-chloronapthelene yielded an analytical sample of Tetrakis-4:5-dimethylphthalocyanine. This compound was somewhat greener than tetrakis-4-methylphthalocyanine, and the metallic reflex was not so pronounced. Its visible spectrum was of the same form as the tetrakis-4-methyl derivative, but with the bands showing a further bathochromic shift. It was less soluble even than phthalocyanine, being only very sparingly soluble in 1-chloronaphthalene, and quite insoluble in pyridine. It sublimed very slowly at 450°, 10^{-6} mm without apparent loss in weight.

(iii) Tetrakis-4:5-dimethylphthalocyanine cobalt (II)

This was the only other member of this series obtained analytically pure, and was prepared by heating together the dinitrile and anhydrous cobalt acetate, and recrystallising the product from pyridine. This gave first tetrakis-4:5-dimethylphthalocyanine pyridine cobalt (II) as a dark blue powder, which on drying at 200° and 15mm pressure lost pyridine equivalent to one mole to give tetrakis-4:5-dimethylphthalocyanine cobalt (II) as dark blue prisms with a purplish reflex. It is more soluble in hot 1-chloronapthelene than the metal free but is completely deposited on cooling. It is quite easily recrystallised from boiling pyridine in which it dissolves to give an intense blue solution, but is however, only sparingly soluble in the cold.

(iv) Tetrakis-4:5-dimethylphthalocyanine nickel (II)

Colaïtis(31) prepared the copper derivative by heating 4:5-dimethylphthalic anhydride with urea and copper bronze in a covered vessel. The preparation was repeated at two different temperatures, using anhydrous nickel acetate in place of copper bronze No pigment was isolated.

(v) Tetrakis-4:5-dimethylphthalocyanine copper (II)

This compound was first prepared in an impure form by de Diesbach and von der Weid(2), during an unsuccessful attempt to prepare 4:5-dimethylphthalonitrile. They sealed 4:5-dibromo o-xylene, cuprous cyanide and pyridine in a tube, and heated the mixture under pressure. The blue pigment which was isolated, they mistakenly identified as a complex between two moles of the dinitrile, two moles of pyridine and one of copper. As was mentioned in (iv) above, Colaitis(31) prepared the pigment from 4:5-dimethylphthalic anhydride by the urea melt technique, and was able to recrystallise it from 1-chloronapthalene.

Three attempts were made to obtain this compound in a pure form, and in each case advantage was taken of the solubility of the metal free compound in 1-chloronapthalene. Tetrakis-4:5-dimethyl phthalocyanine was extracted into a suspension respectively of cupric acetate, copper bronze and finally cuprous chloride, in this boiling solvent. In the first case the product was shown by its visible spectrum to be a mixture of the metal free and the copper pigments, the former being present in the largest quantity. Copper bronze was not attacked at all, but cuprous chloride brought about complete metallation of the pigment to give tetrakis-4:5-dimethylphthalocyanine copper (II). The product was purified by boiling with strong ammonium chloride, and then dissolving in and recovering from concentrated sulphuric acid. It was however insufficiently soluble in 1-chloronapthalene to be recrystallised satisfactorily from this solvent. The yield was small, and shown to be impure, and since it was in the form of an amorphous precipitated powder, comment cannot be made on its crystal form. It is, however, greenish blue in colour as opposed to the richer blue of the unsubstituted- and tetrakis-4-methyl analogs, but shows the typical phthalocyanine reflex when rubbed on glass or p.v.c. Its visible and infra red spectra were recorded and will be discussed under the relevant chapters.

(vi) Tetrakis-4:5-dimethylphthalocyanine dichlorotin (IV)

4:5 dimethylphthalonitrile and anhydrous stannous chloride reacted on heating together to give an excellent yield of tetrakis-4:5-dimethylphthalocyanine dichlorotin (IV) Most impurities were removed by extracting the pigment with the usual lower boiling solvents, and also with chlorobenzene, but this did not remove by-products containing tin. Unfortunately it was insufficiently soluble in 1-chloronapthalene to be recrystallised satisfactorily, and an attempt to sublime it at 450°, 10^{-5}mm led to much decomposition. Some material, however, did come over, and this was analysed and found to be impure. The pigment is green in colour, and shows a bluish reflex when rubbed.

D. Summary of the tetrakis-4:5-dimethylphthalocyanines

These pigments are readily formed in good yield from the dinitrile, and metal salts, and as far as can be seen are typical of the phthalocyanines in their properties. For example, they show the typical phthalocyanine reflex, are blue to green in colour, and their visible spectra are of the same form as their unsubstituted analogs, though showing a bathochromic shift even greater than the tetrakis-4-methyl series. They can be recovered from solution in concentrated sulphuric acid without appreciable loss in weight, and their infra red spectra are self consistent, though showing some very interesting differences from those of unsubstituted phthalocyanines. They are however, exceedingly insoluble, being even less soluble than the phthalocyanines, and this renders purification very difficult and in some cases impossible. No attempt was made to prepare the zinc, magnesium or iron derivatives but doubtless these would show solubility in pyridine due to the formation of pyridinates, and hence could be crystallised from that solvent.

E. Experimental section

Pinacol hydrate and anhydrous pinacol (67), (68)

This preparation was carried out exactly as described by Adams and Adams in "Organic Syntheses"(55), only the scale was increased. Magnesium (80g) was reacted with mercuric chloride (90g) and anhydrous acetone (600g, 758ml) in dry benzene (1,000ml), yielding on work up pinacol hydrate, (450g). This was added to benzene (1,000ml) and the mixture distilled on a steam bath, the water being discarded, and the benzene being repeatedly returned to the flask until no more water came over. The resulting solution was distilled, the fraction boiling between 150° and 180° being collected. This was refractionated to give anhydrous pinacol, 190g, 48% overall boiling 168-78°, 758mm.

2:3-dimethylbutadiene (71)

45% hydrobromic acid (6ml) was added to anhydrous pinacol (190g) and pinacolone (20g, by-product from above preparation), and the mixture gently distilled using an efficient fractionating column, so that the distillate collected at about 60 drops/min. After three and a half hours, the temperature at the still head had risen to 95° and the distillation was stopped. The organic layer of the distillate was washed twice with 50ml portions of distilled water, and dried over calcium chloride; quinol (0.25g) being added as a stabilizer. The product was distilled to yield 2:3-dimethylbutadiene, 74g, 52%, boiling 68-75°/771.4mm.

4:5-dimethyl-1:2:3:6-tetra hydrophthalic anhydride (72)

Maleic anhydride (85g) was dissolved with picric acid (120mg) in boiling benzene (290ml) and the solution cooled to room temperature. Dimethylbutadiene (74g) was added, and when the reaction had subsided the solution was refluxed for 20 hours, evaporated to dryness, and the product recrystallised from petroleum ether (b.p.100-120°). Yield 105g, 66% mp 76.5°, Lit 77-8°(57).

Calc. for $C_{10}H_{12}O_3$:

C = 66.67, H = 6.71, O = 26.62

Found : C = 66.59, H = 6.72, O = 26.43 %

4:5-dimethylphthalic anhydride (74)

The tetrahydro anhydride (100g) was dissolved in glacial acetic acid (180ml) just below its boiling point, and a solution of bromine

(230g, 75ml) in glacial acetic acid (210ml) added over 60 min. It was refluxed for five hours, the AcOH pumped off, and the residue heated at 220° for nine hours. It was recrystallised from petroleum ether (100-120°).

Yield 50g, 51% m.p. 208.5°, Lit(31) 198°

Calc. for $C_{10}H_8O_3$:

C = 68.15, H = 4.58, O = 27.25

Found : C = 68.08, H = 4.75, O = 27.48 %

4:5-dimethylphthalimide (79)

4:5-dimethylphthalic anhydride (40g) was mixed to a slurry with 0.880 ammonia (40ml) and slowly heated over 80 min to 280°, when the mass fused. A sample was recrystallised from ethanol.

Yield 36g, 91% m.p. 238° Lit(2) 240-1°

Calc. for $C_{10}H_9NO_2$:

C = 68.58, H = 5.14, N = 7.80, O = 18.27

Found : C = 67.17, H = 5.51, N = 7.44, O = 19.42 %

4:5-dimethylphthalamide (80)

4:5-dimethylphthalimide (35g) was mixed to a slurry with 0.880 ammonia (125ml) and stirred at room temperature for 24 hours. The product was highly insoluble and could not be recrystallised satisfactorily.

Yield 35g, 91%

4:5-dimethylphthalonitrile (81)

The diamide (35g) was heated to 100° in suspension in pyridine (500ml) and a rapid stream of phosgene was passed through until the mass had solidified (90 min), and the product left to stand for 60 min. It was worked up with crushed ice, neutralised to congo red with conc. HCl and the product isolated by continuous ether extraction. A sample was recrystallised from ethanol and then petroleum ether ($80-100^{\circ}$) to give small plates.

Yield 10g, 35% m.p. 178°.

$C_{10}H_8N_2$ requires :
C = 76.90, H = 5.16, N = 17.94
Found : C = 76.60, H = 4.99, N = 17.74 %

Cyclisations using sodium sulphide (90), (103)

4:5-dimethylphthalonitrile (0.6g) was dissolved in 2-ethoxy ethanol (10ml) and added hot to a solution of anhydrous sodium sulphide (0.054g) in the same solvent (5ml). The resulting solution was heated at 100° in a stoppered tube for 3½ hours. No pigment was isolated.

The dinitrile (1.56g) was dissolved in boiling 2-methoxy ethanol (1.8g, 130°). To this was added 69% aqueous $Na_2S.9H_2O$ (5 drops) and the solution boiled for two hours. A solution of sodium hydroxide (0.15g) in water (2.8ml) was added and the mixture heated at 100° for two hours. It was filtered, the residue being washed with water and acetone, and it was then refluxed for two 18 hour periods, first with acetone and then with chlorobenzene. It was once more filtered, washed with acetone and analysed:

$C_{40}H_{34}N_8$ requires :
C = 76.62, H = 5.47, N = 17.89
Found : C = 73.31, H = 5.38, N = 16.09 % + ash

Tetrakis-4:5-dimethylphthalocyanine (159)

4:5-dimethylphthalonitrile (2.0g) was dissolved in n-amyl alcohol, and a solution of sodium (0.4g) in the same solvent (10ml) added. The mixture was boiled for fifteen minutes, cooled, diluted with ethanol (200ml) and filtered. Yield crude Me_8Na_2Pc, 600mg 28%. The product was boiled for eighteen hours with a mixture of AcOH (80ml) conc. HCl (50ml) and water (30ml), after which some sodium was still present. Hence it was boiled with glacial acetic acid for two days and left to stand for fourteen days. The residue was boiled with distilled water, dried, and recrystallised by extraction with boiling 1-chloronapthalene to give small blue/green prisms. Yield 260mg, 13% overall.

$C_{40}H_{34}N_8$ requires :
C = 76.66, H = 5.46
Found : C = 76.38, H = 5.37 %

Tetrakis-4:5-dimethylphthalocyanine cobalt (II) (179), (179A)

4:5-dimethylphthalonitrile (1.0g) was intimately mixed with cobalt acetate (0.3g, dried at 120° for 1 hour) and the mixture immersed in a Wood's metal bath at 280°. After half an hour, the blue mass was worked up in the usual fashion and recrystallised from pyridine. Yield 416mg of monopyridinate, 34%. This was recrystallised from pyridine twice more to give a blue powder, and analysed:

$C_{45}H_{37}CoN_9$ requires :

$C = 70.87, H = 4.89, N = 16.52$

Found : $C = 70.53, H = 5.14, N = 16.97$ %

The bulk of the sample was dried at 200°, 15mm to give pure tetrakis-4:5-dimethylphthalocyanine cobalt (II) as coppery prisms.

Required loss in weight, 9.64%; found, 9.65%

$C_{40}H_{32}CoN_8$ requires :

$C = 70.26, H = 4.72, N = 16.40$

Found : $C = 70.44, H = 4.67, N = 16.85$ %

(The Nitrogen analysis was performed at the Chesterford Park Research Station)

Tetrakis-4:5-dimethylphthalocyanine nickel (II) (76)

4:5-dimethylphthalic anhydride (7g), anhydrous nickel acetate (1.4g) and urea (10g) were heated together in a covered vessel for three hours. In the first run a temperature of 220° was used, and although on work up with ethanol and acetone a greenish brown powder was isolated this was not a phthalocyanine. In the second run, the mixture was heated at 180° and this time all that was obtained was a charred brown mass.

Tetrakis-4:5-dimethylphthalocyanine copper (II) (164), (181)

The metal free pigment (50mg) was mixed with dried cupric acetate (0.5g) and the mixture shaken with 1-chloronapthalene (50ml). The suspension was refluxed for 1½ hours, filtered, the residue heated at 100° with concentrated HCl for 3 hours, washed well with water and then acetone. Yield 47mg - mostly starting material.

The metal free pigment (36mg) was extracted into a suspension of copper bronze (50mg) in boiling 1-chloronapthalene (50ml) and refluxing continued for four hours. The unmetallated starting material was recovered.

This was repeated, only using cuprous chloride (100mg) in place of the copper bronze. The product was filtered off, washed with ethanol and acetone, heated with saturated aqueous NH_4Cl at 100° for two days, filtered and washed. It was taken up in concentrated sulphuric acid, filtered, poured on to crushed ice, filtered, washed well with water and ethanol and dried. Yield 25mg 46% overall.

$C_{40}H_{32}CuN_8$ requires :

$C = 69.80, H = 4.69, N = 16.28$

Found : $C = 60.42, H = 4.41$ %

Tetrakis-4:5-dimethylphthalocyanine dichlorotin (IV) (93)

4:5-dimethylphthalonitrile (3g) was finely ground with anhydrous stannous chloride (1.0g) and the mixture immersed in a Wood's metal bath, maintained at 220°. When the contents of the flask had reached

215°, the temperature rose rapidly to 282°. the melt becoming pasty, and finally solidifying. Heating was continued for a further 15 min, the product cooled and finely ground. It was extracted over night with benzene, then for 24 hours with acetone, and finally for 24 hours with chlorobenzene, the green product being finely ground between each extraction.

Yield 3.25g, 81%

A sample was sublimed at $450°/10^{-5}$mm, but this was accompanied by much decomposition. Some of the sublimed product was washed with acetone and analysed:

$C_{40}H_{32}N_8Cl_2Sn$ requires:

C = 59.01, H = 3.97, N = 13.76, Cl = 8.70

Found : C = 57.94, H = 3.82, N = 12.30, Cl = 6.30 %

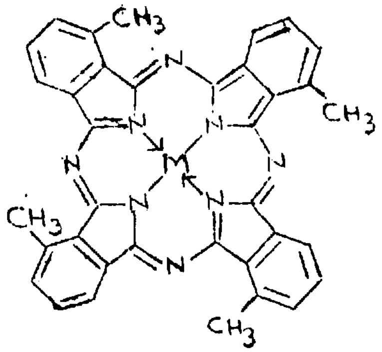
CHAPTER 5

3-METHYLPHTHALONITRILE, AND THE TETRAKIS-3-METHYLPHTHALOCYANINES.

A. Introduction

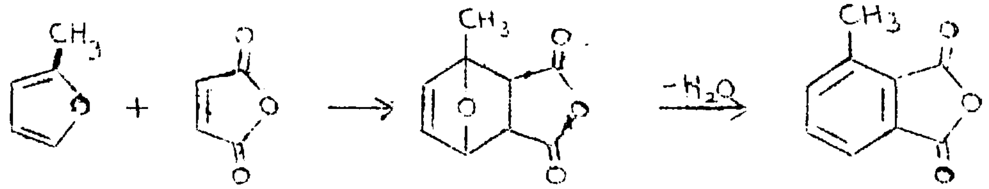
The 3 and 6 positions of the o-phenylene rings in the phthalocyanine molecule are more sterically hindered towards electrophilic attack than are the 4 and 5 positions, as was demonstrated in Chapter 1. However, phthalocyanines with functions in the 3, or 3 and 6 positions, can be synthesised by cyclising the corresponding substituted phthalic anhydrides, or phthalonitriles, the success of the reaction depending upon the bulk of the substituents, and the degree of freedom with which they can move to prevent steric overcrowding. For instance, Haworth and his co-workers prepared tetrakis-3-phenylphthalocyanine copper(II) from 3-phenyl phthalonitrile, and showed this to be different from the product obtained from 4-phenylphthalonitrile(58). This demonstrates that phenyl migration had not accompanied cyclisation. Shigemitsu(43) prepared all eight chloro derivatives of phthalic anhydride, and successfully cyclised all but the 3:4:5:6-tetrachloro derivative to their corresponding copper phthalocyanines, using the urea melt technique. The tetrachloro derivative gave a product identical with that obtained by cyclising 3:4:5-trichlorophthalic anhydride, thus showing that four chlorines have been eliminated - those in the 6 positions. Hexadecachlorophthalocyanine copper(II) can be prepared however, by the chlorination of tetrakis 3:6-dichlorophthalocyanine copper(II) (59).

The purpose of this piece of work was to synthesise 3-methylphthalonitrile and hence the hitherto unknown tetrakis-3-methylphthalocyanines, and to compare their properties with the derivatives in the 4-methyl series. Bearing in mind the **similar** radii of the chlorine atom and the methyl group, it was assumed that 3-methylphthalonitrile would cyclise preferentially to give the symmetrical isomer of the macrocycle.

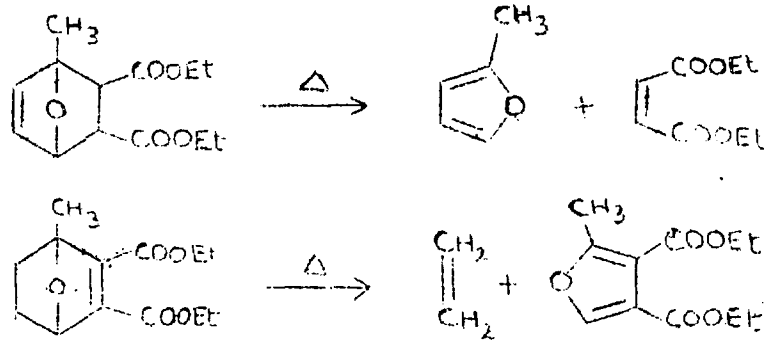


B. The adduct between 2-methylfuran and maleic anhydride

2-methylfuran reacts readily with maleic anhydride in ether solution to give 3-methyl-3:6-endoxo-1:2:3:6-tetrahydrophthalic anhydride(60). It was intended that this adduct should be dehydrated to give 3-methylphthalic anhydride, which could be converted to the nitrile in the usual fashion:-



Van Campen and Johnson(61), record having dehydrated this adduct "by heating with a solution of hydrogen bromide in glacial acetic acid", but give no experimental details. The adduct was re-prepared in good yield, and experiments were carried out to find the best conditions for dehydration. Heating under reflux with 20% hydrogen bromide in glacial acetic acid for one hour yielded a brown polymeric tar, as did a 5% solution after fifteen minutes on a steam bath. When however a 1% solution was used, and heating continued for eighteen hours at 100°, a large quantity of white solid was deposited, which after purification was identified as fumaric acid. It was apparent that a reverse Diels-Alder reaction was taking place under these conditions, the brown tar presumably being a polymer of 2-methylfuran. Further evidence came from the N.M.R. spectrum of the adduct in deuterochloroform, for this not only showed bands corresponding to the adduct, but also those of maleic anhydride and 2-methylfuran in a one to one ratio. The integral of the spectrum showed that there was 45% of the adduct in solution, 55% of it having been dissociated into its two components, presumably by traces of acid in the solvent (trichloracetylchloride, or phosgene?). This assumption was confirmed when the spectrum was run again, this time in acetone. The only bands in the spectrum were those of the adduct. The catalytic effect of traces of acid upon the adduct was demonstrated in the following manner. The infra red spectra of maleic anhydride, of 2-methylfuran and also of the adduct were recorded in analar chloroform. A trace of hydrogen chloride was added to the solution of the adduct, and its spectrum re-recorded after five, fifteen, fortyfive and ninety minutes. Bands appeared at 840, 890cm^{-1} and the carbonyl bands moved to lower wave numbers, showing the presence of maleic anhydride. Also, bands appeared at 1450, 1520 and 1600cm^{-1} characteristic of 2-methylfuran, and these decreased in intensity after some time, as brown colour developed in the solution, due to polymensation. Consequently, it was concluded that acids reverse this particular Diels-Alder reaction, and are of little use as dehydrating agents. Some work by Alder and Rickert(62) was later noted, demonstrating the anomolous behaviour of endoxo-cyclohexene dicarboxylic acid derivatives under conditions of pyrolysis, two examples of which are shown:



Even under these conditions, the formation of a substituted furan takes precedence over aromatisation of the six membered ring. Attention was turned to an alternative route to 3-methylphthalonitrile.

C. The Diene synthesis

1:3-pentadiene reacts with maleic anhydride to give an adduct(63) which can be aromatised to 3-methylphthalic anhydride, and hence converted to the dinitrile. 1-penten-3-ol was prepared by the action of ethylmagnesium bromide on acrolein(64), and converted to 3-acetoxy-1-pentene, using the method of Marvel and his co-workers(65) by refluxing with acetic anhydride and a catalytic quantity of pyridine. Kepner(66) obtained 1:3-pentadiene by pyrolysing 1-penten-3-ol over heated alumina, but it had been found (see Chapter 7) that better yields of dienes are obtained by pyrolysing acetates, and this was the method adopted(67). The acetate was added dropwise to the top of a vertical heated silica tube, packed with glass beads, the gases issuing from the bottom being condensed. Several runs were carried out varying the rate of addition, the temperature, and the size of the glass beads. The results are listed in Table III.

Table III

Vol. Acetate Added	Vol Acetate Recovered	Diameter Glass-beads	Temp.	Rate of Addition	Vol. Diene	Yield (on Acetate cracked)
80ml	62ml	3.0mm	400-20°	40drops/min	3ml	25%
250ml	165ml	3.0mm	420°	22drops/min	17ml	34%
227ml	145ml	3.0mm	430-40°	20drops/min	23ml	39%
140ml	100ml	0.3mm	410-30°	19drops/min	11.5ml	42%
100ml	50ml	0.3mm	450-60°	26drops/min	14.5ml	42%

It is apparent that higher temperatures, lower addition rates and larger surface area of the column packing give the best yields. The diene was reacted with maleic anhydride to give 3-methyl-1:2:3:6-tetrahydrophthalic anhydride, aromatised to 3-methylphthalic anhydride with bromine in glacial acetic acid, converted via 3-methylphthalimide to 3-methylphthalamide in the usual fashion with 0.880 ammonia, and finally dehydrated with phosgene in pyridine to give 3-methylphalonitrile. The nitrile showed C≡N absorption in the infra red at 2240cm^{-1}.

D. The Tetrakis-3-methylphthalocyanines

(i) Tetrakis-3-methylphthalocyanine

This was prepared by the action of sodium *n*-amyloxide on 3-methylphthalonitrile in boiling *n*-amyl alcohol. The resulting tetrakis-3-methylphthalocyanine disodium was demetallated by refluxing with glacial acetic acid and the tetrakis-3-methylphthalocyanine so obtained was recrystallised from o-dichlorobenzene to give dark blue needles with a coppery reflex. Although it was recrystallised three times, and also sublimed, a satisfactory analysis could not be obtained, the compound analysing as though it had two extra methyl groups present. They were certainly not present on the periphery of the molecule, as some metallated derivatives of the correct composition were prepared from this sample. Alternatively it is difficult to believe that they could be attached to the central nitrogen atoms, since the N-H stretching frequency in the infra red at 3246cm^{-1} is present, and is not reduced in intensity when compared with the corresponding band in other metal-free phthalocyanines. The only satisfactory way of settling this problem would be to plot the complete structure of the molecule by X-ray analysis. The pigment is less soluble than tetrakis-4-methylphthalocyanine, but dissolves in boiling o-dichlorobenzene to give a greenish blue solution.

(ii) Tetrakis-3-methylphthalocyanine iron (II)

3-methylphthalonitrile reacts with ferric acetate at 290° to give tetrakis-3-methylphthalocyanine iron (II). As was the case with the tetrakis-4-methyl derivative, this compound was not obtained analytically pure, but was converted by treatment with methanolic potassium cyanide to dipotassium [tetrakis-3-methylphthalocyaninedicyano ferrate (II)] in order to establish the structure of this series of substituted phthalocyanines by study of the N.M.R. spectrum. (See Chapter 8.). Tetrakis-3-methylphthalocyanine iron(II) was also prepared by extracting the metal-free pigment into a suspension of anhydrous ferric chloride in o-dichlorobenzene. When ferric acetate was used, however, the metal free pigment was recovered unchanged.

(iii) Tetrakis-3-methylphthalocyanine cobalt (II)

The reaction between cobalt acetate and 3-methylphthalonitrile at 240° yielded tetrakis-3-methylphthalocyanine cobalt (II). Several recrystallisations were necessary to obtain an analytical sample. As is usually the case with cobalt phthalocyanines, this sample showed a greater solubility than the copper derivative (iv), and could be recrystallised from pyridine. It forms dark blue prisms with a reddish reflex

(iv) Tetrakis-3-methylphthalocyanine copper (II)

The metal free pigment was extracted into a suspension of cupric acetate in boiling o-dichlorobenzene to give a good yield of *tetrakis-3-methylphthalocyanine copper (II)* The action of cupric acetate on 3-methylphthalonitrile, as described above for the cobalt derivative gave a very impure product which could not be purified satisfactorily. The pigment was obtained as a blue powder with a slight greenish tint, which gave a coppery reflex when rubbed on glass. It showed little solubility in chlorobenzene.

(v) Tetrakis-3-methylphthalocyanine zinc

Zinc reacts readily with 3-methylphthalonitrile at high temperatures to give *tetrakis-3-methylphthalocyanine zinc*. This was prepared as the anhydrous material by drying a recrystallised sample at 200°, 10mm, being a dark blue powder and showing a reddish reflex when rubbed on glass. It is more soluble than any of the other metal derivatives prepared, and can be recrystallised from chlorobenzene and from pyridine in which it is very soluble. It is not as soluble as the 4-methyl derivative, however.

(vi) Tetrakis-3-methylphthalocyanine dichlorotin (IV)

3-Methylphthalonitrile was heated with anhydrous stannous chloride at 220° in the usual manner for preparing dichloro stannic derivatives. The reaction was strongly exothermal, the temperature of the melt rising to 310°, and work up in the usual fashion yielded *tetrakis-3-methylphthalocyanine dichlorotin (IV)* as a light green powder. Carbon and hydrogen analysis of this compound gave considerable trouble, several ignitions of the same sample giving figures ranging from 56.5 to 60.0% for carbon. Since successful analyses were obtained on other tetrakis-3-methylphthalocyanines before, during, and after the several attempts carried out on the derivative in question, it was assumed that it was particularly difficult to combust. Nitrogen and chlorine analyses gave no trouble.

E. Summary of the tetrakis-3-methylphthalocyanines

The synthesis of 3-methylphthalonitrile by the diene route was quite straightforward, and most stages went in good yield. The dinitrile reacts with a variety of metal salts, and some metals to give reasonably good yields of the corresponding macrocycles, but better yields are available by the action of metal salts on the metal free pigment. For a given derivative, members of this series are intermediate in solubility between the unsubstituted phthalocyanines and the 4-methyl series, being generally soluble in o-dichlorobenzene, and in the cases of the ferrous, cobalt and zinc derivatives, in pyridine also. Visible absorption spectra in these solvents are of the usual form for phthalocyanines, but show a bathochromic shift of the lines, greater even than that of the tetrakis-4:5-dimethyl series.

The disodium derivative was very difficult to demetallate, more so than the corresponding tetrakis-4-methyl disodium derivative, and

and there seems to be connection here with the relative bathochromic shifts in the visible spectra. This will be discussed in Chapter 10. The compounds crystallise well, but not so well as the unsubstituted phthalocyanines, and all show a characteristic coloured reflex.

F. Experimental section

3-methyl-3:6-endoxo-1:2:3:6-tetrahydrophthalic-anhydride (110),(131)

Maleic anhydride (102g) was dissolved in anhydrous ether (750ml) and a trace of azobisisopropylcyanide added. 2-methylfuran (85g, 92.5ml; purified by passing through alumina column, and redistilling) was added, and the mixture left to stand for six days. The product was filtered and evaporated to dryness, and recrystallised with difficulty from ethyl acetate. Yield 160g, 85%, m.p. 81°. Lit.(60) 84°.

Action of acid on the 2-methylfuran adduct (118), (127)

(i) A sample of the adduct was dissolved in a boiling solution of hydrogen bromide (20%) in glacial acetic acid, and the solution refluxed for one hour. The solvent was boiled off under reduced pressure to yield a dark brown tar.

(ii) The adduct was heated at 100° with a 5% solution of hydrogen bromide in glacial acetic acid for fifteen minutes. Removal of the solvent yielded once more a dark brown tar, and some unchanged starting material.

(iii) The adduct (120g) was added to a 1% solution of hydrogen bromide in glacial acetic acid (250ml) and heated on a steam bath at 100° for 18 hours. The fine white precipitate was filtered off and washed with acetic acid. Yield 40g, 64%. This was recrystallised from benzene/ethanol, to give a white powder, subliming at 247°. The N.M.R. spectrum showed a broad band at 2.6τ and a sharp one at 3.30τ, and the u.v. spectrum a band at 205mμ, $E_{max} = 22,500$ It was identified as fumaric acid.

Calc. for $C_4H_4O_4$:

C = 41.37, H = 3.48, O = 55.15

Found : C = 41.38, H = 3.57, O = 53.52 %

1-Penten-3-ol (130), (134)

Ethyl magnesium bromide was prepared by the action of ethyl bromide (115g, 80ml) in anhydrous ether (250ml) on magnesium turnings (25g) covered with anhydrous ether (110ml). When all the magnesium had dissolved, the mixture was cooled to -15° (ice and salt) and a solution of acrolein (50g, 60ml) in anhydrous ether (250ml) added dropwise with vigorous stirring. Stirring was continued for 18 hours, during which time the mixture returned to room temperature, and the product was worked up with ammonium chloride (60g) in water (150ml), the ether layer separated, and the pasty residue washed twice with ether (100ml portions). The combined ether layers were dried (Na_2SO_4), evaporated down, and the 1-penten-3-ol distilled under reduced pressure. Yield 45g, 58.5%, b.p. 41°/31mm. A sample was redistilled at atmospheric pressure. B.p.113.8°/763mm; $n_D^{25} = 1.4219$. Lit. b.p.114-4.6°/760mm(66); n_D^{20} 1.4240(68)

Calc. for $C_5H_{10}O$:

$C = 69.71, H = 11.70$

Found : $C = 69.24, H = 11.60$ %

3-Acetoxy-1-pentene (135), (136)

1-Penten-3-ol (106g) was dissolved in acetic anhydride (367g, 338ml), and pyridine (1ml) added. The solution was heated on a steam bath at 100° for 18 hours. The product was shaken with cold water (700ml), the top layer being separated and shaken first with a solution of sodium carbonate (30g) in water (350ml) and then with water (400ml). It was dried over anhydrous sodium sulphate, and distilled under reduced pressure. Yield 128g, 85%, b.p.44.5°/29.5mm. A sample was redistilled at atmospheric pressure. B.p. 131-2°/763.4mm; $n_D^{22.5}$1.4100; Lit$^{(69)}$. B.p. 131-3°/760mm; n_D^{20}1.4139.

Calc. for $C_7H_{12}O_2$:

$C = 65.59, H = 9.43, O = 24.98$

Found : $C = 66.19, H = 9.70, O = 24.58$ %

1:3-Pentadiene (161)

Only one out of five runs is described, namely the run which gave the highest yield. The apparatus consisted of a vertical silica tube (90 x 2.5cm), fitted at the top with a dropping funnel and an inlet for nitrogen gas. The bottom of the tube was fitted with a condenser, and a receiver immersed in 'cardice'. The tube was packed with glass beads (0.5cm, to a depth of 2cm , 0.03cm to a depth of

46cm and 0.5cm, to a depth of 20cm), and heated by an electric winding. The tube was heated to 450-60°, a slow stream of nitrogen passing through (20mls/min) and 3-acetoxy-1-pentene (100ml) added to the top at a rate of 26 drops a minute. The issuing gases were condensed, washed twice with water (25ml), once with saturated sodium bicarbonate solution (25ml), dried over magnesium sulphate and distilled. 50ml of unchanged starting material was recovered. Yield of diene, 14.5ml, 10.1g 42%
Boiling range 38-46°

3-Methyl-1:2:3:6-tetrahydrophthalic anhydride (162)

Maleic anhydride (40g) was dissolved in benzene (150ml), picric acid added (50mg) and the solution cooled to room temperature. 1:3-pentadiene (37.5g, 54ml) was added, and when the reaction had subsided, the yellow solution was refluxed for 18 hours. The solvent was evaporated, and the product recrystallised from petroleum ether (40-60°). Yield 63g, 84%; m.p.62°. Lit(63) 61-2°.

Calc. for $C_9H_{10}O_3$:
$C = 65.05, H = 6.07$
Found : $C = 64.91, H = 5.93$ %

3-Methylphthalic anhydride (163)

3-Methyl-1:2:3:6-tetrahydrophthalic anhydride (60g) in glacial acetic acid (120ml) was oxidised in the usual fashion by bromine (150g, 51ml) in glacial acetic acid (120ml). The product was recrystallised from petroleum ether (80-100°).

Yield 25g, 43%, m.p.117-8°, Lit(69) 115°.

Calc. for $C_9H_6O_3$:

$C = 66.67$, $H = 3.72$,

Found : $C = 66.36$, $H = 3.66$ %

3-Methylphthalimide (167)

3-Methylphthalic anhydride (24g) was mixed with 0.880 ammonia (25ml) to give a homogeneous syrupy solution. This was slowly heated over three hours until the temperature had reached 285° when the mass fused. The product was dissolved in acetone (800ml) boiled and filtered through charcoal, and the solution evaporated to dryness. Yield 21g, 88%. A sample was recrystallised from petroleum ether (80-100°) m.p.193-3.5°, Lit(70) 187°.

Calc. for $C_9H_7NO_2$:

$C = 67.08$, $H = 4.37$, $N = 8.69$, $O = 19.86$

Found : $C = 67.63$, $H = 4.35$, $N = 8.58$, $O = 19.72$ %

3-Methylphthalamide (169)

3-Methylphthalimide (20g) was stirred for 60 hours with 0.880 ammonia solution (65ml). The product was filtered off and dried. Yield 17.5g, 80%. A sample was recrystallised twice from ethanol/water (10:1) m.p. 207-8°.

$C_9H_{10}N_2O_2$ requires :

$C = 60.66$, $H = 5.65$, $N = 15.72$, $O = 17.96$

Found : $C = 60.53$, $H = 5.50$, $N = 15.97$, $O = 17.94$

3-Methylphthalonitrile

3-Methylphthalamide (17g) was suspended in hot pyridine (250ml) at 100°, and a rapid stream of phosgene was passed for 100 min, with vigorous stirring until the mass had set solid. It was worked up with crushed ice, neutralised to congo red with concentrated hydrochloric acid, and extracted with ether for three days.

Yield 10.9g, 79%. A sample was recrystallised from petroleum ether (100-120°), m.p.147°, Lit$^{(71)}$ 143°.

Calc. for $C_9H_6N_2$:

C = 76.05, H = 4.25, N = 19.70

Found : C = 75.70, H = 3.65, N = 19.57 %

Tetrakis-3-methylphthalocyanine (175)

3-Methylphthalonitrile (2.5g) was refluxed with a solution of sodium (0.5g) in n-amylalcohol (25ml) for fifteen minutes. The product was filtered hot, washed well with acetone and then ethanol. It was then suspended in glacial acetic acid (50ml) and water (5ml) and boiled under reflux for three days, during which time the colour changed from royal blue to a light peacock blue. The finely divided product was filtered off washed with water and then acetone.

Yield 486mg, 19.5%. It was recrystallised twice from o-dichlorobenzene, analysed (i), recrystallised from o-dichlorobenzene analysed (ii), sublimed at 400°, 10^{-6}mm, and analysed again (iii).

$C_{36}H_{26}N_8$ requires :

C = 75.76, H = 4.59, N = 19.65

Found (i) : C = 76.21, H = 5.25, N = 17.15

Found (ii) : C = 76.52, H = 4.55

Found (iii) : C = 76.37, H = 4.90, N = 18.77

$C_{38}H_{30}N_8$ requires:

C = 76.23, H = 5.05, N = 18.72 %

Tetrakis-3-methylphthalocyanine iron (II) (176), (178)

3-Methylphthalonitrile (0.65g) was mixed with excess ferric acetate (0.3g) and heated at 290° for 35 min. The product was worked up in the usual fashion. Yield 260mg, 37%. It was recrystallised twice from chlorobenzene, once from pyridine and dried at 200°/10mm.

$C_{36}H_{24}FeN_8$ requires :

C = 69.25, H = 3.87

Found : C = 64.01, H = 4.11 %

A second sample was prepared by extracting tetrakis-3-methylphthalocyanine (70mg) into a suspension of ferric chloride (50mg, anhydrous) in o-dichlorobenzene (50ml). It was recrystallised from o-dichlorobenzene.

Tetrakis-3-methylphthalocyanine cobalt (II) (172)

3-Methylphthalonitrile (1.0g) and anhydrous cobalt acetate (0.4g) were heated together at 240° for 30 min. The product was worked up in the usual fashion. Yield 605mg, 55%. It was recrystallised three times from chlorobenzene, analysed (i), recrystallised from pyridine, dried at 200°C, 15mm and analysed again (ii).

$C_{36}H_{24}CoN_8$ requires :

$C = 68.93, H = 3.85, N = 17.83$

Found (i) : $C = 68.34, H = 3.92, N = 16.81$

Found (ii) : $C = 68.55, H = 4.55, N = 18.28$ %

Tetrakis-3-methylphthalocyanine copper (II) (171), (198)

(i) 3-Methylphthalonitrile (1.0g) was reacted with anhydrous cupric acetate (0.4g) exactly as above. The product after work up was twice recrystallised from o-dichlorobenzene. Yield 655mg, 59%

$C_{36}H_{24}CuN_8$ requires :

$C = 68.42, H = 3.82$

Found : $C = 67.64, H = 4.13$ %

(ii) Tetrakis-3-methylphthalocyanine (100mg) was extracted into a suspension of cupric acetate (50mg) in chlorobenzene (50ml) and the mixture refluxed for 24 hours. The product on cooling was filtered off, washed with acetone, refluxed for two days with saturated aqueous ammonium chloride, and twice recrystallised from o-dichlorobenzene. Yield 100mg, 90%

$C_{36}H_{24}CuN_8$ requires :

$C = 68.42, H = 3.82, N = 17.72$

Found : $C = 68.40, H = 3.95, N = 17.70$ %

This analysis was carried out at the Chesterford Park Research Station.

Tetrakis-3-methylphthalocyanine zinc (174)

3-Methylphthalonitrile (1.0g) and zinc dust (0.2g) were heated together at 250° for twenty minutes. After work up the product was recrystallised four times from chlorobenzene, and dried at 200°/10mm for one hour. Yield 128mg, 10%

$C_{36}H_{24}N_8Zn$ requires :

$C = 68.20$, $H = 3.80$, $N = 17.67$

Found : $C = 68.06$, $H = 3.73$, $N = 17.95$ %

The nitrogen analysis was carried out at the Chesterford Park Research Station.

Tetrakis-3-methylphthalocyanine dichlorotin (IV) (173)

Stannous chloride (0.5g) and 3-methylphthalonitrile (1.0g) were heated together at 220°. The temperature of the melt rose rapidly to 310°, and the product solidified. After a further fifteen minutes, the green solid was worked up in the usual fashion, and recrystallised three times from o-dichlorobenzene. Yield 0.95g, 71%.

$C_{36}H_{24}Cl_2N_8Sn$ requires :

$C = 57.02$, $H = 3.19$ $Cl = 9.35$, $N = 14.79$

Found : $C = 57.46$, $H = 2.80$, $Cl = 9.65$, $N = 14.79$ %

CHAPTER 6

SOME STUDIES OF DERIVATIVES OF PHTHALOCYANINE TIN (IV)

A. Introduction

While carrying out their earlier work on the metal derivatives of phthalocyanine, Linstead and his co-workers(27) observed that phthalocyanine aquohydroxyaluminium (III) and phthalocyanine dihydroxy tin(IV) both react with sodium hydroxide to give sodium salts. An example is disodium {phthalocyanine dioxostannate (IV)]. They explained this behaviour in terms of the amphoteric nature of aluminium, and stannic hydroxides. Later work by Elvidge and Lever(54), however, showed that both phthalocyanine aquohydroxychromium (III) and phthalocyanine dihydroxymanganese (IV) act as dibasic acids towards sodium hydroxide, forming disodium salts. It is apparent that a different explanation is required here. Elvidge and Lever explained this acidity in terms of 'perpendicular conjugation' - that is, stabilisation of the formal negative charge on the oxygen atoms of the anionic species, by conjugation through a right angle to the π electron system of the phthalocyanine ring, using empty d orbitals of the metal atom. They proposed that the $4d_{xz}$ (and $4d_{yz}$) orbitals of chromium and manganese atoms have the correct symmetry, and are also sufficiently diffuse to overlap respectively the p_x (and p_y) orbitals of the oxygen atoms and the p_z orbitals of the nitrogen atoms, attached to the metal(72)(73)(54). This concept accounts for the formation of anionic species in the phthalocyanines of chromium (III) and manganese (IV) (and also, for example, dipotassium [phthalocyanine dicyanoferrate (II)]), as well as explaining the hypsochromic shift in the absorption spectra of these compounds.

The purpose of the following work was to attempt to establish whether derivatives of phthalocyanine tin (IV) are stabilised to any degree by perpendicular conjugation.

Also included in this chapter are some observations on the stability of diphthalocyanine tin (IV).

B. Phthalocyanine dichlorotin (IV)

The chlorine atoms attached to the tin in the title compound are known to be labile, and so it was reasoned that they should react with grignard reagents to give alkyl or aryl tin compounds. If perpendicular conjugation were possible at the tin atom, then the visible absorption spectrum of a derivative such as phthalocyanine diphenyltin (IV) would be expected to show differences from that of the parent compound, greater than those due to inductive effects. In view of the very low solubility of phthalocyanine dichlorotin (IV) it was first of all necessary to find a suitable solvent for a grignard reaction, which was also an ether. The best solvents for phthalocyanines are those which are aromatic, slightly polar, and of molecular weight about 150. 2-Furfuryloxytetrahydropyran was prepared by the method of Forrest Woods(74), but was found to be a poor solvent. 1-Methoxynaphthalene(75) was comparable with 1-chloronaphthalene as a solvent, but great difficulty was encountered in removing the last traces of 1-naphthol. These traces interfered seriously with the grignard reaction since they gave rise to a strong blue colour, which masked the colour changes of the tin derivative. Diphenyl ether was a good solvent above 160°, and could easily be freed from traces of phenol, but had the disadvantage of having a relatively high melting point (28°). Nevertheless, it was used as the solvent in the following studies. A saturated solution of phthalocyanine dichlorotin (IV) was prepared at 80° in diphenyl ether, on the test tube scale, and to this was added a slight excess of phenylmagnesium bromide in the same solvent. A series of colour changes were observed; blue green to reddish purple, changing on shaking in air through claret once more to blue green. After being left to stand over night at room temperature the solution was bright yellow green in colour, and its visible absorption spectrum is compared below with that of the starting material; points of inflection being denoted (i) :

$SnCl_2Pc$ λ max: 6010(i), 6250, 6650(i), 6940
Product (1) λ max: 6160(i), 6470, 6790, 7230
$\Delta\lambda$: +150, +220, +140, +290 Å

Although the soret band (3500Å) of the product (1) was masked by impurities, the rest of its spectrum was characteristic of a phthalocyanine. When this reaction was carried out on a larger scale using boiling solutions of reagents, in an attempt to isolate a product, a band was once more observed in the visible spectrum at 7230Å, but this disappeared during subsequent work up. A few milligrams of a product (2) was isolated by precipitating solids from the diphenyl ether solution with a large excess of diethyl ether, and extracting this residue with benzene on a soxhlet. The visible spectrum of this product (2) is given below, compared once again with phthalocyanine dichlorotin(IV) :

$SnCl_2Pc$ λmax : 3570, 6010(i), 6250, 6650(i), 6940
Product (2) λmax : 3640, 6000(i), 6320, 6700(i), 7010
$\Delta\lambda$ + 70, - 10, + 70, + 50, + 70 Å

The bathochromic shifts of the lines of product (1) are much greater than those of product (2).

A final run was carried out using tetrakis-4-methylphthalocyanine dichlorotin (IV), since this compound shows a greater solubility in diphenyl ether. This time an excess of phenyl magnesium bromide was added to a solution of the phthalocyanine in diphenyl ether at room temperature, the major reaction being reduction of the pigment to tetrakis-4-methylphthalocyanine tin (II). However, a small peak was observed in the visible spectrum at 7360Å, this disappearing on addition of ethanol :

$(4\text{-}Me)_4SnCl_2Pc$: 3675, 5980(i), 6150(i), 6410, 6830(i), 7130
Product (3) : ~3450, 5730(i), 5960(i), 6190, 6580, 6860, 7360
+ Ethanol : ~3450, 5730(i), 5960(i), 6190, 6580, 6860 Å

The peak at 7360Å is very significant, and ties in well with that at 7290Å observed in product (1). The difference in wavelength of 70Å is in keeping with the bathchromic shift generally observed on substituting phthalocyanines with four 4-methyl groups (see Chapter 10). In view of the very dilute solutions employed in these experiments, it was virtually impossible to prevent side reactions from taking place. For example, the reduction of tin (IV) by excess grignard and the hydrolysis of any aryl tin derivatives by moisture or other hydroxylic derivatives was a constant problem, but fortunately product (1) was not apparently sensitive to aerial oxidation.

A close examination of the results obtained by Elvidge and Lever$^{(54)}$ for derivatives of phthalocyanine chromium (III) shows that functional groups attached to the central metal atom bring about shifts in the visible spectra to both shorter and longer wavelengths depending on the nature of the substituent. However, even when perpendicular conjugation is postulated, these shifts are rarely greater than 70Å, so it seems reasonable to suppose that product (2) is a derivative of phthalocyanine tin(IV) with two substituents attached to the metal, other than chlorine atoms. The shifts of respectively 290 and 230Å observed in products (1) and (3), however, demand some alternative explanation. Ring substitution of phthalocyanine, especially in the 3-positions, brings about quite large bathochromic shifts in the visible spectrum. For example phthalocyanine dichlorotin (IV) is compared below with tetrakis-3-methylphthalocyanine dichlorotin (IV) :

$SnCl_2Pc$ λmax : 3570, 6010(i), 6250, 6650(i), 6940

$(3\text{-}Me)_4SnCl_2Pc$ λmax : 3651, 6210(i), 6466, 6940(i), 7213

$\Delta\lambda$: + 81, + 200, + 216, + 290, + 273 Å

- and as can be seen, the shifts are of the right order. None the less, it is difficult to accept that a grignard reagent could bring about substitution on a benzene ring, and even if this were the case, the product would not be labile to hydroxylic reagents. The only feasible explanation is that the phenyl substituents are attached to the tin atom, and are undergoing conjugation with the phthalocyanine ring with far greater efficiency than for example the oxyanions in disodium [phthalocyanine oxohydroxochromate (III)]. The reason for saying this is because the phenoxide anion shows a greater bathochromic shift in its ultraviolet spectrum when compared with benzene than does diphenyl; but here apparently a perpendicularly conjugated phenyl group shows a larger shift than a perpendicularly conjugated oxygen anion.

It is important at this stage to consider whether perpendicular conjugation at a four-valent octahedrally substituted tin atom is theoretically possible. The configuration of tin in the ground state, above the M shell is :

$$4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^2\ 5d^0$$

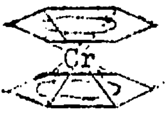
and that of the stannic cation :

$$4S^2\ 4p^6\ 4d^{10}\ 5s^0\ 5p^0\ 5d^0$$

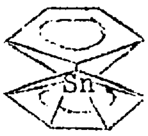
and consequently an octahedral four valent tin complex would be an outer orbital complex, using $5s\ 5p^3\ 5d^2$ hybrid orbitals.

This leaves the 4f, the 6s and three of the 5d orbitals free, all of which are of roughly the same energy in tin. The 6s and $5d_{xy}$ orbitals can be eliminated on symmetry grounds, and in view of the very diffuse nature of the $\overset{5}{\cancel{4}}d_{xz}$ and $5d_{yz}$ orbitals, it is unlikely that these would overlap the $2p_z$ orbitals of the central nitrogen atoms of the phthalocyanine nucleus, to any appreciable extent. The only alternative mechanism for perpendicular conjugation, therefore, is the use of 4f orbitals, and certain of these may indeed have the correct symmetry, as well as being less diffuse than the 5d orbitals. This explanation is attractive as complexes using 4f orbitals are virtually unknown, but it does not fully account for the large bathochromic shift in the visible spectrum.

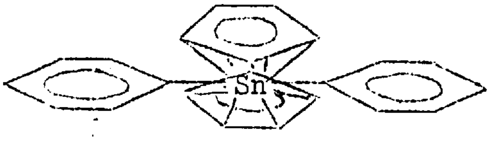
There is an alternative, though equally hypothetical explanation, which uses a concept other than perpendicular conjugation. The action of phenylmagnesium bromide on chromium (III) chloride, followed by reduction, gives the sandwich compound dibenzene chromium(76) :



Among many other similar known complexes are dicyclopentadienyl tin (II)(77) and dicyclopentadienyl diphenyl tin (IV)(78), with the following structures :



and



It is just possible that product (1) was a similar 'sandwich' compound, phthalocyanine dibenzenetin (II), the tin having been reduced, perhaps by excess grignard reagent, to the divalent state. It is not proposed to discuss the nature of the bonding in such a complex, as this still has to be settled for dicyclopentadienyl iron (II) - ferrocene - the best characterised of the 'sandwich' compounds. However, what is required is the interaction of one π electron system with another to give the necessary bathochromic shift in the visible spectrum, and such a complex may have the correct parameters.

It must be emphasised again that both of the suggestions put forward in this section as to the nature of product (1) are pure surmise, and are not based on any experimental evidence apart from the observed large shift in the bands of the phthalocyanine visible spectrum. Obviously, a satisfactory systematic study of this problem cannot be made until a derivative of phthalocyanine dichlorotin (IV) is prepared, which shows a considerably greater solubility in lower boiling ethers. This conclusion, together with the desirability of having a general synthesis for alkyl substituted phthalocyanines, led to the work described in the next chapter. Before this is considered, however, some studies of diphthalocyanine tin (IV) are included here for convenience.

C. Diphthalocyanine tin (IV)

This compound was first prepared by Barrett and his co-workers(27) by the reaction between phthalocyanine disodium and phthalocyanine dichlorotin (IV), and its visible spectrum was later recorded by Whalley(50). The purpose of repeating this work was to obtain a crystalline sample, suitable for an X-ray crystallographic examination. The method of Barrett was repeated, the crude reaction product being filtered and concentrated in the recommended fashion, and the deposited solid extracted into benzene. Whalley recommends that the benzene solution should be chromatographed on alumina, using benzene-methanol (20 : 1) as an eluant, in order to separate phthalocyanine and phthalocyanine dichlorotin (IV) from the required product. This was tried, but it was found that a quantity of greenish tarry material came off the column with the diphthalocyanine tin (IV), and it proved very difficult to separate the two. However, when pure benzene was used as an eluant, without methanol being added, the greenish tar remained on the column, in spite of the fact that a very much larger volume of eluant was required. After two recrystallisations on a soxhlet the product was deposited as fine needles, it being recrystallised twice more before being analysed. Crystals of a suitable size for X-ray measurements were 'grown' by taking up about fifty milligrams of the needles in a large volume of benzene, in a beaker covered with a clock glass, and allowing this to evaporate to dryness at room temperature over a period of about three weeks. It was noted that this process brought about considerable decomposition of the product, only about half being recovered. This observation was confirmed in a repeat run. A standard solution of diphthalocyanine tin in benzene was also found to 'go off' after several days standing at room temperature. The absorption bands in the visible spectrum slowly decreased in intensity, two new bands appearing at 6985 and 6595 Å increasing in intensity for the first eight days, reaching a maximum after twelve days and then they too began to decrease. The first of these bands, however, was twice as intense as the second. The most reasonable explanation is that the diphthalocyanine tin (IV) is decomposing into a mixture of phthalocyanine and a derivative of phthalocyanine tin (IV). The former has two bands of roughly equal intensity to the 6260Å band of diphthalocyanine tin (IV) at 6980 and 6650Å and experience has shown that derivatives of phthalocyanine tin (IV) have a band around 7000Å of greater intensity, and one of low intensity around 6300Å. The summation of these bands should give a pattern similar to the one observed, the maximum after eight days probably being due to super saturation of the benzene with the relatively insoluble products, this being followed by précipitation, and hence decrease of the maxima. Kroenke and Kenney(79) observed that a sample of diphthalocyanine tin (IV), when subjected to a temperature of 560° for 45 min decomposed into phthalocyanine and phthalocyanine tin (II), but in the case discussed above, conditions were favourable for the tin to retain its four valent state.

The complete structure of diphthalocyanine tin (IV) is being determined by X-ray crystallography.

D. Experimental section

2-Furfuryloxytetrahydropyran

Furfurylalcohol (196 g) was mixed with dihydropyran (168 g), and concentrated hydrochloric acid (0.5 ml) added with shaking at room temperature. The temperature of the mixture rose to 110° and the brownish liquid was allowed to stand over night. It was twice distilled from sodium hydroxide pellets, under reduced pressure, the main fraction being collected at 70°, 0.08 mm. Yield 145 g, 40%. Lit.(74) 34%.

1-Methoxynaphthalene (55)

The method used was a modification of that of Hiers and Mager(75) for preparing anisole. 1-naphthol (1000 g) was dissolved in a solution of sodium hydroxide (360 g) in water (3 litres). Dimethylsulphate (900 g) was added with stirring at $< 10^\circ$ over a period of two hours, and the product left to stand over night. The top oily layer was separated, the lower layer being shaken with benzene, and the benzene extract combined with the oil. This was washed with water, dried over calcium chloride and distilled twice under reduced pressure.

Yield 885 g, 80%, b.p. 68°, 0.4 mm.

The redistilled product was yellow in colour, and the presence of 1-naphthol was indicated by the formation of a strong brown colour with phenyl diazonium chloride, and a red-brown colour with ferric chloride. The 1-naphthol was removed by shaking an ethereal solution of the ether with portions of 2N sodium hydroxide solution until the bottom layer remained colourless. The top red layer was then washed with water and redistilled. However, on standing, the yellow colour once more developed, and 1-naphthol was detectable.

Phthalocyanine diphenyltin(IV) (52)(109)

(i) Phthalocyanine dichlorotin (IV) (ca. 5 mg) was boiled with diphenyl ether (10 ml), and the cooled solution decanted from deposited crystals. A few drops of a solution of phenyl magnesium bromide in diethyl ether was added. The blue green solution turned to reddish purple, changing on shaking in air through claret, and back to blue green again. After standing over night, the colour was yellow green, the solution containing product (1).

(ii) Phthalocyanine dichlorotin (IV) (300 mg) was taken up in boiling diphenyl ether (220 ml) and the solution cooled to 160°. Bromobenzene (1.0 g) was added to a suspension of magnesium turnings (200 mg) in anhydrous diethyl ether (10 ml), and when the reaction had ceased, diphenyl ether (10 ml) was added, and the diethyl ether removed under reduced pressure. The resulting solution of phenyl magnesium bromide was added all at once to the hot phthalocyanine dichlorotin (IV) solution, the resultant mixture rapidly cooled and left to stand over night. This solution showed a shoulder in the visible spectrum at 7230Å, but the principal band was at 6990Å. Diethyl ether (500 ml) was added, the precipitated solids being filtered at the pump and extracted with benzene on a soxhlet. The extract was evaporated to dryness and once more extracted, yielding about 5 mg of a blue solid - product (2).

(iii) (i) was repeated using a cold saturated solution of tetrakis-4-methylphthalocyanine dichlorotin (IV) in diphenyl ether, only this time rather more phenyl magnesium bromide was added. The observed colour changes were bright green to bluish violet, turning on exposure to air to blue green. This solution - product (3) - showed a band at 7360Å in the visible spectrum, the remainder of the bands being assignable to tetrakis-4-methylphthalocyanine tin (II). Addition of ethanol (2 ml) removed the band at 7360Å.

Diphthalocyanine tin (IV) (82)(91)

Sodium (1.8 g) was dissolved in n-amyl alcohol (100 ml, dried over BaO and redistilled), and the solution raised to just below its boiling point. To this was added phthalonitrile (20 g, recrystallised from benzene), the solution refluxed for 10 min filtered hot, and the solid extracted on a soxhlet with benzene (sodium dried) over night. The resulting phthalocyanine disodium was dried in an oven (100°) and used in this state for the next stage.

Phthalocyanine dichlorotin (IV) (1.0 g) was added to 1-chloronaphthalene (180 ml) and refluxed for 20 minutes after which phthalocyanine disodium (0.8 g) was added, and refluxing continued for 90 minutes. The solution was cooled, filtered free from solids (180 mg sodium chloride, 470 mg phthalocyanine), evaporated down to 20 ml at a water pump, cooled and added to a soxhlet thimble. This was extracted for 24 hours with benzene (500 ml), the solution cooled, filtered free from solids, and run on to an alumina column (5 x 12 cm). When eluted with benzene-methanol (20 : 1), the column developed into a strongly absorbed green band at the top (phthalocyanine), a slow moving green band (a little phthalocyanine dichlorotin (IV)) and a rapidly moving dark blue band, contaminated with some green material. When, however, the column was eluted with pure benzene (3 litres) the dark blue band came off relatively free from green tar, though a large quantity of eluant was required. The eluate was evaporated to dryness, and the blue solid twice extractionally crystallised on a soxhlet with benzene (150 ml), after which the product was isolated as fine coppery needles. It was recrystallised twice more and analysed.

Calc. for $C_{64}H_{32}N_{16}Sn$:

C = 67.18, H = 2.82, N = 19.60, Sn = 10.37

Found : C = 67.26, H = 3.06, N = 19.94, Sn = 10.59 %.

CHAPTER 7

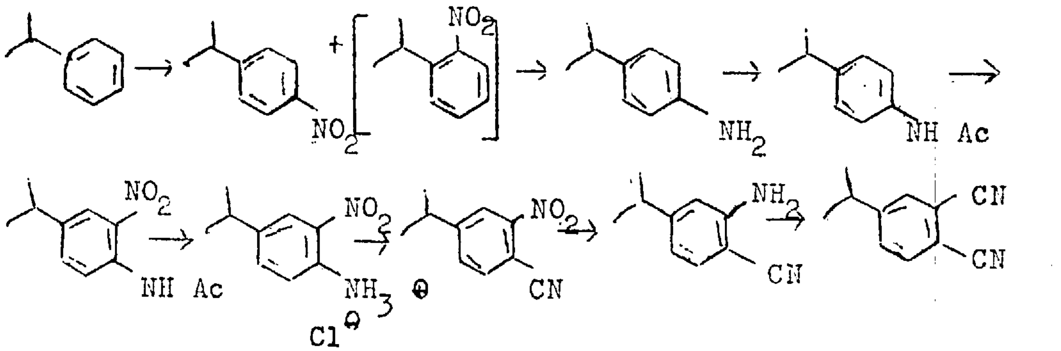
THE GENERAL SYNTHESIS OF TETRAKIS-4-SUBSTITUTED PHTHALOCYANINES

A. Introduction

Many problems in phthalocyanine chemistry, such as nuclear magnetic resonance studies, and the studies of metals with a valency greater than two in a phthalocyanine environment, would be greatly simplified if the pigments could be rendered more soluble in lower boiling solvents. Aliphatic side chains seem to be the most effective solublising functions, as these would be inert to most chemical reagents, and would not interfere seriously with the visible spectrum of the phthalocyanines. The work in Chapters 3, 4 and 5 showed that tetrakis-4-substitution brings about the largest increase in solubility in the case of methyl substituents, so what was required was a general synthesis of 4-alkyl phthalonitriles. The diene synthesis was the most attractive, but in view of the difficulty in preparing 2-substituted butadienes, attention was first turned to the possibility of applying Findecklee's classical synthesis of 4-methylphthalonitrile from toluene(30) to other monoalkylated benzenes.

B. Isopropylbenzene as a starting material

Isopropylbenzene (Cumene) was chosen, since it would lead to 4-isopropylphthalonitrile, the isopropyl group having the advantages of being bulky and non-symmetrical, both of these characteristics being desirable. The synthetic route was planned as follows, the first five stages being described by Haworth and Barker(80), and the last three based on the synthesis of 4-methyl phthalonitrile, described by Morgan and Coulson(81) and Findecklee(30):



Haworth and Barker record yields of 90% of para- and 7% of orthonitrocumenes from the low temperature nitration of cumene with a mixture of concentrated sulphuric and nitric acids. The best yield of the para-isomer found in practice was 51%, and this was mixed with the orthonitro-, 2:4-dinitro- and 2:4:6-trinitro derivatives. The reaction was carried out by adding the cumene to the acid mixture cooled in ice and salt, so that the reaction temperature did not vary outside the limits -1° to +6°. After work up, the p-nitrocumene was isolated by fractional distillation under reduced pressure. Care was required here, because of the presence of higher nitrated derivatives, for in one instance explosive autoxidation took place when air was admitted, after distillation, to the still-hot distillation flask.

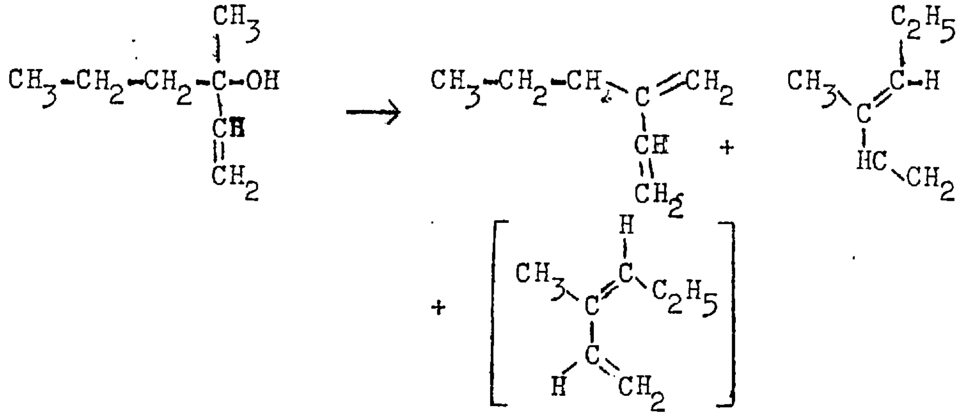
p-Aminocumene was prepared in 90% yield on the small scale, by hydrogenating the p-nitro compound over raney nickel (W4). When this reaction was carried out on a large scale, however, trouble was encountered because of inefficient stirring, and two consecutive hydrogenations of the same sample only resulted in about 15% reduction.

At this stage it was felt that it would be more profitable to investigate possible general routes to 2-alkyl butadienes, rather than to continue with the synthesis under discussion, since this latter was showing signs of being very time consuming, with little prospect of getting a good yield of 4-isopropylphthalonitrile.

C. Synthetic routes to 2-alkyl butadienes

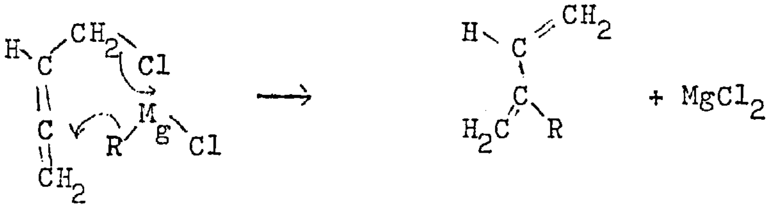
Before discussing possible routes individually, it is useful to list those that appear in the literature, with a few comments about each.

1. The dehydration of tertiary allylic alochols over 20% zirconia on pumice at 290-300°, or over magnesium sulphate at 300° (82). This method gives two isomeric dienes, although three are theoretically possible; for example from 3-methyl-1-hexen-3-ol :-



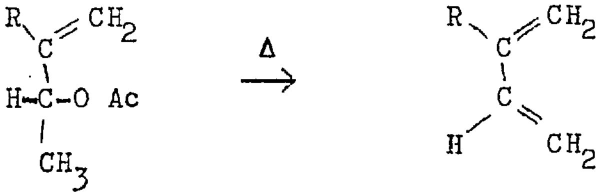
2. The cracking of tertiary allylic acetates over glass beads at 480 - 90° (83). Once again, three isomeric dienes are theoretically possible.

3. The action of a grignard reagent on 1-chloromethyl allene, below 40° (84). This method is specific, but there are side reactions :



4. The action of a grignard reagent on 2-chloro butadiene (85). This method is also specific, but there are several side reactions, making for difficulty in the separation of the diene.

5. The cracking of secondary allylic acetates over glass beads at 400 - 20° (65). Probably the most satisfactory specific method.



Specific methods are always desirable, since they do away with the necessity of separating isomers. In methods 2 and 3 however this advantage is offset by the production of by-products of similar boiling point to that of the diene, and also by the inconvenient methods of preparation of the starting materials. Method 5 uses an aldehyde with four or more carbon atoms as a starting material and involves a Mannich reaction followed by a Hofmann- and then a grignard reaction, to give a secondary allylic alcohol. This is acetylated and then cracked. The method is without doubt the most satisfactory route to 2-alkyl butadienes, but was unfortunately discovered too late to be used in this work. Methods 1. and 2. were the ones adopted, since both involved the synthesis of tertiary allylic alcohols which are quite readily available, and also, judging by Nazarov's observations(82), the diene mixtures could be separated without too much difficulty. Normant(86)(87) prepared tertiary allylic alcohols by the action of vinyl magnesium chloride on methyl alkyl-ketones, whereas Nazarov added acetylene to methyl alkyl-ketones and reduced the resulting acetylenic alcohols with hydrogen, using palladium on calcium carbonate as a catalyst(83). Both of these preparations depend on the availability of methyl alkyl-ketones, but the action of alkyl grignard reagents on methyl vinyl ketone offers a more general synthesis.

In view of the ready availability of methyl *iso*butyl-ketone it was decided that attempts should be made to prepare 2-*iso*butylbutadiene and hence tetrakis-4-*iso*butylphthalocyanine and its derivatives. It was also felt that the synthesis of tetrakis-*n*.butylphthalocyanine as a comparison would give some useful information on the effects of side chain branching on the solubility of phthalocyanines, and consequently attempts were made to prepare 2-*n*.butylbutadiene from methyl vinyl-ketone, since methyl *n*.butyl-ketone is not readily available.

D. The route to 2-*n*.butylbutadiene

Coburn(88) prepared 2-penten-3-ol by the action of methyl magnesium bromide on crotonaldehyde. This method was adapted to the synthesis of 3-methyl-1-hepten-3-ol, using the reaction between *n*-butylmagnesium bromide and methyl vinyl ketone, which is isomeric with crotonaldehyde. Several runs were carried out, and the results are listed in Table IV.

Table IV

Run	Mole ratio Grignard/ Ketone	Temp.	Solvent	Stabilizer	Product
1	1 : 1	> 25°	Ether	-	Very high boiling yellow oil
2	1 : 1	18°	"	-	5ml, b.p.150°, 760mm very impure
3	1.25 : 1	-18°	"	-	15ml,b.p.60-70°, 25mm very impure
4	1.25 : 1	-33°	"	-	17ml,b.p. 64°, 27mm + ketone
5	2 : 1	-42°	"	Quinol	17ml,b.p. 67°,28.5mm + ketone
6	2 : 1	-25°	T.H.F.	Quinol	25ml,b.p.64-6°, 22mm + ketone

The reaction was without success, there being a large number of major side reactions unless low temperatures were used, and the ketone added very slowly to an excess of grignard. Polymerisation of the ketone was inhibited to a certain extent by the addition of quinol, and tetrahydrofuran (T.H.F.) was found to be a better solvent than ether; but even at very low temperatures there were still two main reactions taking place. A study of the infra red spectra of the products from runs 4, 5 and 6 showed that an allylic alcohol was present (bands at 3460, 3075, 1830, 1635, 992 and 918 cm^{-1}), contaminated with a large quantity of a saturated aliphatic methyl ketone (bands at 1705, 1360 cm^{-1}). This observation was confirmed by the N.M.R. spectrum (60 Mc) there being a triple quartet AMX system of bands, typical of a vinyl group adjacent to a tertiary carbon atom, and another band assignable to a methyl group adjacent to a ketone carbonyl :

CH_3-C=O	7.95 τ	
A	5.06 τ	JAM = 2.0 cps
M	4.90 τ	JMX =17.7 cps
X	4.13 τ	JAX =10.0 cps

All attempts to separate the alcohol from the ketone, by slow fractional distillation resulted in mixed fractions containing more or less of one particular product. Also acetylation of the mixture with acetic anhydride and pyridine to produce the allylic acetate, only served to raise the boiling point of the alcohol from a little below, to a little above that of the ketone, so a separation could not be achieved here, either. The ketone was identified from the melting points of its semicarbazone and 2 : 4-dinitrophenyl hydrazone derivatives, and proved to be methyl-*n*-hexyl ketone (2-octanone). It is interesting to note that the reaction between *n*-butyl magnesium bromide and methyl vinyl ketone leads equally favourably to both normal- and Michael-addition to the α-β unsaturated system, since both acrolein (see Chapter 5) and crotonaldehyde give only allylic alcohols. This is unforunate, since separation of the two products on the large scale is impracticable, and so this route had to be abandoned.

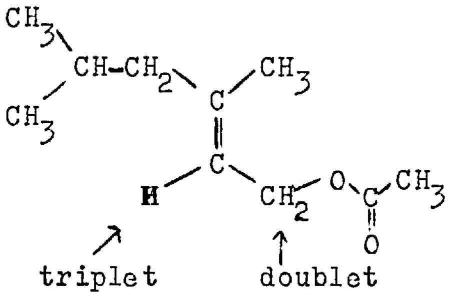
E. The route to 2-*iso*butylbutadiene

(i) 3:5-dimethyl-1-hexyn-3-ol was prepared in 55% yield by the action of sodium acetylide on methyl *iso*butyl ketone in liquid ammonia, the method used being a modification of that described by Heilbron(89). Linstead, Elvidge and Whalley(90) recommend distilling the crude product under reduced pressure from a little anhydrous potassium carbonate, to remove traces of acid. This was found to be very satisfactory, but it was noted that distillation from the carbonate at atmospheric pressure led to decomposition of the alcohol back to acetylene and methyl *iso*butyl ketone. Redistillation of the pure alcohol at atmospheric pressure in the absence of potassium carbonate gave no trouble. The structure of the alcohol was confirmed by N.M.R. studies, there being in the spectrum two bands, among others, of equal intensity, and each equivalent to one proton, at 7·90 and 7·56τ. It was uncertain which should be assigned to the hydroxyl and which to the acetylenic protons, so a sample was reacted with acetic anhydride in the presence of a little pyridine to give 3-acetoxy-3:5-dimethyl-1-hexyne. The band at 7.56τ was found to have moved to 7.52τ, so was assigned to the acetylenic proton, the band at 7.90τ being replaced by one three times as intense at 8.02τ, due to the acetoxy methyl group, and thus assignable to the hydroxy proton.

(ii) Nazarov and Mavrov(82) reduced tertiary acetylenic alcohols to the corresponding allylic derivatives in 75% yield by hydrogenation at three atmospheres pressure using 2% palladium on calcium carbonate as a catalyst. This method was modified for the reduction of 3 : 5-demethyl-1-hexyn-3-ol, hydrogenation being carried out in ethanol solution at atmospheric pressure, using 2% palladium on strontium carbonate as a catalyst. The reaction was stopped when one mole of hydrogen had been taken up to give 90% yield of 3 : 5-dimethyl-1-hexen-3-ol. The structure of this compound was confirmed by infra red (bands at 3420, 3080, 1835, 1635, 995 and 920 cm^{-1}) and N.M.R. spectroscopy at 60 Mc, the latter showing the allylic AMX system of three quartets, very similar to the set observed in 3-methyl-1-hepten-3-ol:

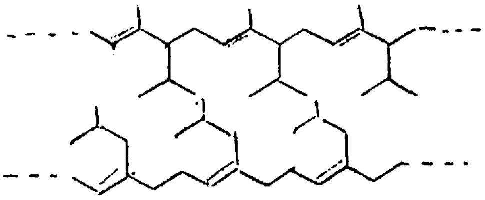
A	4.95τ	JAM	1.8 cps
M	4.78τ	JMX	17.6 cps
X	4.00τ	JAX	10.4 cps

(iii) Acetylation of the allylic alcohol with acetic anhydride in the absence of pyridine, gave a product which lacked the expected AMX system of twelve bands in the N.M.R. spectrum. Instead, there was a triplet at 4.74τ equivalent to one proton, and a doublet at 5.50τ (J = 7.3 cps) equivalent to two. It appears that an allylic re-arrangement has taken place, to give 1-acetoxy-3:5-demethyl-2-hexene :



Acetylation in the presence of pyridine, however, led to the expected product, 3-acetoxy-3:5-dimethyl-1-hexene, although this was contaminated with some unchanged alcohol. It showed bands in the infra red at 1720, and 1240 cm^{-1} (acetoxy group) and also at 3060, 1835, 1635, 990, 915 cm^{-1} (vinyl group), there being a band at 3480 cm^{-1} due to the presence of some alcohol.

(iv) Dehydration of the allylic alcohol. Nazarov and Mavrov(82) dehydrated 3:4-dimethyl-1-penten-3-ol by passing the vapour over 20% zirconia supported on pumice at 300°, to give a mixture of 2-isopropylbutadiene (58%) and 3:4-dimethylpentadiene (30%), which was separated by fractional distillation. As far as was possible these conditions were applied to the dehydration of 3:5-dimethyl-1-hexen-3-ol, the vapour being passed from a still pot up a column containing the catalyst, maintained at about 300°, the issuing gases being condensed. Much gas was evolved, presumably being low boiling hydrocarbons, including ethylene, and an appreciable quantity of methyl isobutyl ketone was isolated from the distillate. However, the distillate, after being freed from water, was shown from its infra red spectrum to contain dienes, and was fractionated at atmospheric pressure using a column of 25 plate efficiency (with respect to benzene/carbon tetrachloride). Fractions boiling between 100 - 120° all contained dienes (infra red bands at 3080,1800, 1635, 1590, 995 and 900 cm^{-1}) and ketone (band at 1710 cm^{-1}); and vapour phase chromatography showed the presence of anything between two and five components in fractions. The purest fraction isolated, boiling at 108°/765 mm contained ketone, and a diene which was identified from its N.M.R. spectrum by comparison with dienes prepared in later work, as <u>3 : 5-dimethyl-1 : 3-hexadiene</u>. A syrupy, benzene-soluble polymer was isolated from the still pot when the fractional distillation was completed, and after purification, it was shown to be a polymer of a C_8H_{14} unit containing 13 - 14 units per chain. The N.M.R. spectrum in benzene gave little structural evidence except that the polymer was probably a mixture. Two basic series would be expected, with possible combinations of both :



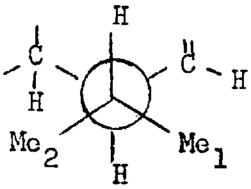
No attempt was made to prepare Diels-Alder adducts of the diene fractions.

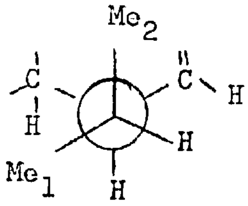
(v) Distillation of the allylic acetate. When the allylic acetate described under (iii) was distilled at 0.55 mm pressure, the liquid nitrogen trap attached to the pump unit became clogged with a white solid. At room temperature this was a liquid smelling strongly of acetic acid, this latter being removed by stirring with anhydrous sodium carbonate. The product after fractional distillation proved from its N.M.R. spectrum to be a mixture of at least two dienes; an observation confirmed by the infra red spectrum which also showed the presence of some ketone (band at 1704 cm^{-1}). Diene formation was probably catalysed by traces of calcium chloride drying agent in the acetate. The olefinic region of the N.M.R. spectrum was too complex to be broken down, but 3 : 5-dimethyl-1 : 3-hexadiene was identified as follows. A complex series of weak bands near 7.40τ, equivalent to one proton was assigned to the 5-hydrogen atom, and a quartet centred at 8.27τ, J=1.2 cps was assigned to the 3-methyl group, undergoing long range trans splitting by the 2- and 4-hydrogen atoms. A singlet at 7.99τ was tentatively assigned to the side chain methylene group of 2-*iso*butylbutadiene, but this would be expected to appear as a double doublet, and not a singlet. This diene mixture was reserved for a Diels-Alder reaction, and is further discussed under section F.

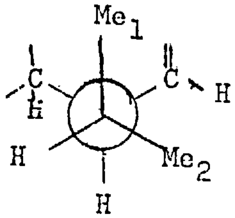
(vi) Pyrolysis of the allylic acetate. 3-acetoxy-3:5-dimethyl-1-hexene was pyrolysed by passing the vapour through a column packed with glass beads at 500°, much as was described in the preparation of 1:3-pentadiene, in Chapter 3, to give 70% of diene fraction based on the acetate cracked. After distillation, the diene fraction was refractionated, and was shown to contain some acetylenic derivative (band in the infra red at 3320 cm^{-1}), a trace of ketone (band at 1710 cm^{-1}) and diene(s) (bands at 3080, 1790, 1640, 1590, 995 and 900 cm^{-1}). The acetylenic derivative was probably an -en -yne derived from 3-acetoxy-3:5-dimethyl-1-hexyne, present in the allylic acetate. By this stage, experience had shown that it was impossible to tell which dienes were present in mixtures from a study of the infra red spectrum, since no diene had been isolated in a pure form. It was hoped that the dienes could be separated as their Diels-Alder adducts, and some degree of success was achieved here (see section G).

F. Derivatives of 3:5-dimethyl-1:3-hexadiene

The diene fraction obtained by distilling 3-acetoxy-3:5-dimethyl-1-hexene under reduced pressure was reacted with maleic anhydride in benzene, to give after work up a low melting white solid. A small sample was sublimed under reduced pressure, and recrystallised from petroleum ether (b.p. 80 - 100°), yielding 3-isopropyl-4-methyl-1:2:3:6-tetrahydrophthalic anhydride, which was identified from its N.M.R. spectrum, therefore establishing the presence of 3:5-dimethyl-1:3-hexadiene in the diene fraction. The only unusual feature of the N.M.R. spectrum of the anhydride was an unsymmetrical triplet (actually a double doublet with one band in common) centred at about 9.9τ and assignable to the gem.-dimethyl groups of the *iso*propyl function. At first sight, a simple doublet would be expected, due to splitting of the two identical methyl groups by the tertiary proton. A closer study, however, shows that the two methyl groups are not equivalent, and this is best illustrated as follows. By looking along the bond joining the *iso*propyl function to the six membered ring in a model of the adduct, consideration of the three 'staggered' conformations shows that at no time do the two methyl groups experience the same magnetic field simultaneously :



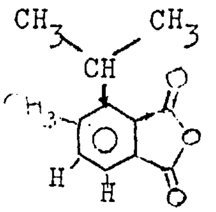


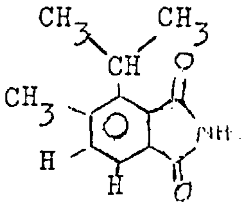


As a result, the two methyls would be split individually to give a double doublet, as observed. This effect is only observed, of course, when for example an *iso*propyl or comparable group is attached to an as~~s~~ymmetric carbon atom.

Oxidation of the Diels-Alder adduct with bromine in glacial acetic acid, yielded *3-isopropyl-4-methylphthalicanhydride* as white slippery plates, the structure being confirmed by N.M.R. This time, the *iso*propyl methyl groups showed up as a doublet, and the tertiary proton as a septet, as expected.

Fusion of the anhydride with 0.880 ammonia in the usual way, gave a good yield of 3-isopropyl-4-methylphthalimide which, like the anhydride, showed a series of three bands in the carbonyl region of the infra red spectrum, respectively at 1752, 1725 and 1690 cm^{-1}. The anhydride absorbs at 1847, 1818 and 1765 cm^{-1}. The N.M.R. spectra of the two compounds had many features in common, and are compared below :





Gem. dimethyl	8.54τ doublet J = 7.2 cps	8.56τ doublet J = 7.4 cps
4-methyl	7.39τ singlet	7.45τ singlet
Tertiary proton	6.07τ septet J = 7.2 cps	6.04τ septet J = 7.4 cps
5- and 6-)) protons)	2.40τ) AB)))J=7.9 cps 2.24τ) quartet)	2.57τ) AB)))J=7.9 cps 2.29τ) quartet)

The imide showed a quite amazing stability towards nucleophilic reagents, being recovered unchanged after stirring with 0.880 ammonia solution for twenty four hours during an attempt to prepare the diamide, and also being unattacked by refluxing with a methanolic solution of sulphuric acid. An attempt to cyclise the imide to a derivative of phthalocyanine copper (II), using the urea melt technique was equally unsuccessful, so it appears that the five membered ring is sterically hindered from opening. The anhydride is, however, converted to the half ethyl ester after being left to stand for several days in dilute ethanol solution, so seems to be more labile than the imide. These steric effects are not unknown with substituted phthalic anhydrides, for Alder and Rickert(91) found that the hydrolysis of diethyl [3-*iso*propyl-6-methylphthalate] led to 3-*iso*propyl-6-methylphthalic anhydride, and not the free acid. A sample of 3:4:5:6-tetramethylphthalic anhydride isolated later (see section G) proved to be exceedingly stable towards hydrolysis, the stability of these anhydrides apparently depending upon the size of the groups in the 3- and ~~5~~ 6-positions, and also upon whether additional groups in the 4- and 5-positions prevent these groups from bending away from the carbonyl functions. The properties of substituted phthalic anhydrides would make a very interesting study. The ultraviolet absorption spectra of several are recorded in Chapter 10.

G. Further derivatives from C_8 dienes

The mixture of dienes obtained by pyrolysing 3-acetoxy-3:5-dimethyl-1-hexene consisted of fractions boiling between 106 - 114° at atmospheric pressure. The lower boiling fractions (106 - 110°) gave a syrupy adduct with maleic anhydride, whereas the higher fractions (113 - 114°) gave mostly a solid. Intermediate fractions gave a mixture of the two which could be separated to a certain extent by filtration by suction. A sample of the solid was recrystallised to constant melting point from petroleum ether (80 - 100°), and analysed as $C_{12}H_{16}O_3$, but the N.M.R. spectrum showed it to be a mixture of 3-isopropyl-4-methyl-1:2:3:6-tetrahydrophthalic anhydride (double doublet centred at 8.98 and 8.87τ) and 4-isobutyl-1:2:3:6-tetrahydrophthalic anhydride (doublet centred at 1.67τ) in proportions of 10:13. Further evidence for the latter came from a quartet in the N.M.R. spectrum of the diene mixture centred at 7.99 , assignable to the side chain methylene of the isobutyl group. This mixture was oxidised with bromine in glacial acetic acid to give the aromatic anhydrides, and these were separated by making use of the stability of the 3-isopropyl-4-methyl derivative towards hydrolysis. Treatment with sodium hydroxide solution followed by ether extraction removed the stable anhydride (which was identified from its infra red spectrum) and left a solution of the sodium salt of 4-isobutyl phthalic acid. The free acid was liberated as a dark brown oil, and an attempt was made to distil it under reduced pressure. This resulted in elimination of water, and reformation of the anhydride as a syrupy oil which was purified by filtering a hot solution in acetone through charcoal. The infra red spectrum of the oil (liquid film) was typical of a phthalic anhydride, with strong bands at 1836, 1765, 1258 and 888 cm^{-1}, though quite different from that of 3-isopropyl-4-methylphthalic anhydride; and it also showed a broad band at about 3000 cm^{-1} and a strong band at 1695 cm^{-1} assignable to the free acid. All attempts to purify this syrup, or to isolate it as a solid by molecular distillation or extraction with various solvents, were without success; and no analysis was carried out, due to the presence of an appreciable quantity of the free acid.

Since only a small amount of this anhydride had been isolated, it was decided that an attempt should be made to cyclise it directly to a derivative of phthalocyanine copper <u>(II)</u>, rather than to complete the synthesis of 4-<u>iso</u>butylphthalonitrile. Dudnikov's version of the urea melt method was used(92), where the anhydride is mixed with urea, a metal salt, and ammonium molybdate, and the mixture slowly heated in suspension in 1:2:4-trichlorobenzene. The method was first tried out on unsubstituted phthalic anhydride, and yielded 80% of phthalocyanine copper <u>(II)</u>; but when applied to the anhydride under discussion, only a few milligrammes of a blue pigment was isolated and that only after careful work up and chromatography on alumina. Although there was too small a quantity for infra red, or microanalysis, the pigment was found to be very soluble in cold benzene, and showed a visible spectrum characteristic of a substituted phthalocyanine. This is compared below with that of phthalocyanine copper <u>(II)</u> :

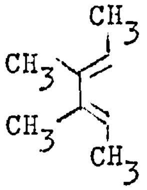
CuPc	λ_{max}:	3500,	5100,	5260,	5670,	5880,	6110,	6480,	6780Å
Derivative,	λ_{max}:	3465,			5730,	5930,	6197,	6577,	6897Å

The bathochromic shift here is greater than that observed in tetrakis-4-methyl- and tetrakis-4:5-dimethylphthalocyanine copper(II though less than that in the tetrakis-3-methyl derivative. The form of the spectrum and the enhanced solubility of the pigment are in keeping with it being <u>tetrakis-4-isobutylphthalocyanine copper (II)</u>, but this cannot be verified until larger quantities are available. The solubility is certainly very encouraging.

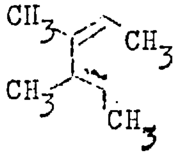
Attention was turned at this point to the syrupy maleic anhydride adduct obtained from the lower boiling fraction of dienes, in the hope that this would yield on oxidation, more 4-*iso*butylphthalic anhydride. Aromatisation with bromine in glacial acetic acid, yielded a very dark solid, much of which failed to dissolve in acetone. That which was in solution was filtered hot through charcoal, and the product recrystallised to yield 3-*iso*propyl-4-methylphthalic anhydride, identical with the samples previously isolated. The dark brown solid which failed to dissolve in acetone was sublimed under high vacuum ($120^{\circ}/10^{-6}$mm), to give white needles, recrystallised from acetone in which they were only sparingly soluble.

This product had an infra red spectrum typical of a phthalic anhydride with three carbonyl bands respectively at 1825, 1790 and 1760 cm^{-1}, and also strong bands at 1195 and 912 cm^{-1}, but was different from that of the two isomers previously isolated. It analysed as $C_{12}H_{12}O_3$ - an isomer of the required derivative - and although its melting point was high ($276-8^{\circ}$), a molecular weight measurement showed it to be a monomer. The N.M.R. spectrum showed two bands of equal intensity at 7.65 and 7.37τ, but no bands in the aromatic region, so it was concluded that the compound was 3:4:5:6-tetramethylphthalic anhydride. Criegee and Knoll(93) prepared this compound by two different routes, and record a melting point of 260° - rather lower than the value found. It therefore seemed necessary to settle its structure by comparison with an authentic sample, prepared by an unambiguous synthesis.

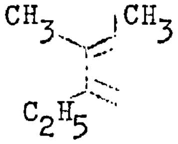
Criegee and Knoll prepared 3:4-dimethyl-trans, trans-2:4-hexadiene by the acid catalysed dehydration of 3:4-dimethylhexane-3:4-diol, condensed this with maleic anhydride, and oxidised the product to 3:4:5:6-tetramethylphthalic anhydride. Gostunskaya, however, dehydrated the diol with acetic anhydride and phosphoric acid, to obtain three other possible isomers, 3:4-dimethyl-cis, trans-2:4-hexadiene, 2-ethyl-3-methyl-1:3-pentadiene and 2:3-diethyl butadiene(94). These are listed below with their physical properties :

1.


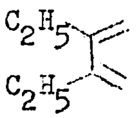
b_{760} 134-5 n_D^{20} 1.4755

2.


b_{760} 114.4 n_D^{20} 1.4410

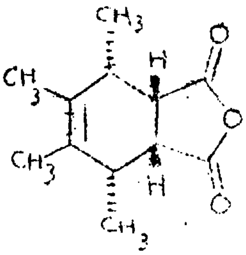
3.


b_{760} 126.3 n_D^{20} 1.4610

4.


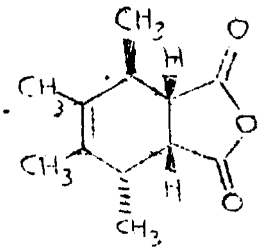
b_{760} 136.3 n_D^{20} 1.4760

The maleic anhydride adducts of dienes (1) and (2) would have the structures :



m.p.113–4° (93)

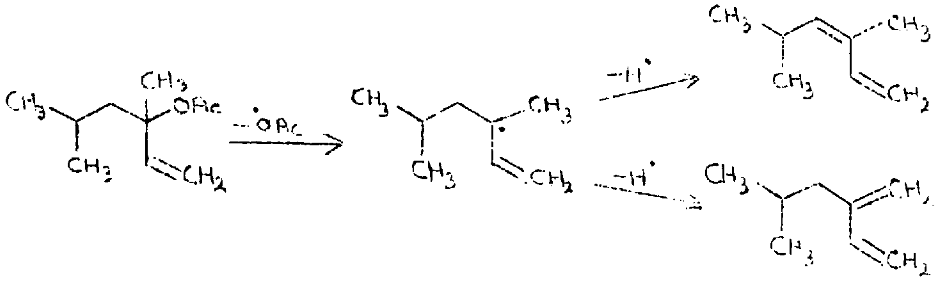
and



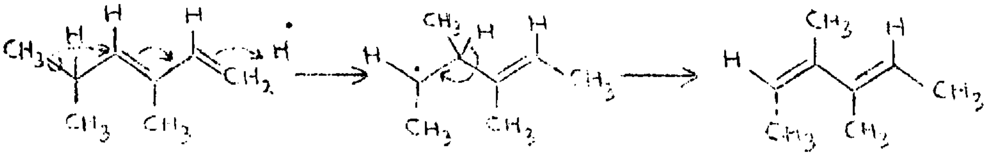
m.p. 46–7° (94)

Judging by the syrupy nature of the adduct isolated, it seems that the second one must have been present, and hence derived from 3:4-dimethyl-*cis*,*trans*-2:4-hexadiene in the original diene mixture. This is in keeping with the low boiling point of this isomer. Both of these adducts, however, can be oxidised to 3:4:5:6-tetramethylphthalic anhydride.

Gostunskaya's method was attempted first, since it was desirable to isolate the dimethyl-*cis*,*trans*-hexadiene and study its N.M.R. spectrum; in order to establish whether it had been present in the original diene mixture isolated from 3-acetoxy-3:5-dimethyl-1-hexene. 3:4-dimethylhexane-3:4-diol was prepared by the reduction of ethylmethyl ketone by magnesium amalgam. This was heated slowly with a four-fold excess of acetic anhydride and a little phosphoric acid as described by Gostunskaya, but all that was isolated was acetic acid and some allylic acetate. No dienes were detected. When, however, the diol was heated slowly with 45% hydrobromic acid as described by Allen and Bell(56) fractional distillation yielded 42% of a diene fraction boiling between 114-135° at 761 mm. The N.M.R. spectra of three fractions showed this to contain dienes (1) and (2) in about equal proportions, and a very small quantity of one or both of the isomers containing ethyl groups (triplet at 8.97τ, J = 7.5 cps, quartet at 7.78τ, J = 7.5 cps). Diene (1) was most easily identified since the 2- and 5-protons appeared as a quartet at 4.93τ, J = 6 cps, the 1- and 6-methyls as a doublet at 8.30τ, J = 6 cps, and the 3- and 4-methyls as a singlet at 8.25τ, apparently not undergoing long range trans-splitting by the 2- and ~~4~~5-protons. Diene (2) gave a much more complex spectrum, all four methyls now being distinguished, and undergoing more or less splitting by the 2- and ~~4~~5-protons. What was important, however, was that these methyl bands in the 8.3 - 8.5τ region and some in the 5.0τ region corresponded quite nicely to unassigned bands in the spectrum of the diene mixture obtained by pyrolysing 3-acetoxy-3:5-dimethyl-1-hexene. A sample of diene (1) was reacted with maleic anhydride to give the expected solid adduct, and this on oxidation with bromine in glacial acetic acid gave 3:4:5:6-tetramethylphthalic anhydride, melting at 276°, and having an infra red spectrum identical with the anhydride tentatively assigned with this structure. This evidence establishes the presence of 3:4-dimethyl-<u>cis</u>,<u>trans</u>-2:4-hexadiene in the mixture obtained from 3-acetoxy-3:5-dimethyl-1-hexene, and it is important to consider next how this could have been formed. The mechanism of the pyrolysis is probably free radical, going in two stages as follows :



Mechanistically, it is most likely that the diene in question is formed from 3:5-dimethyl-1:3-hexadiene by attack by hydrogen free radicals :



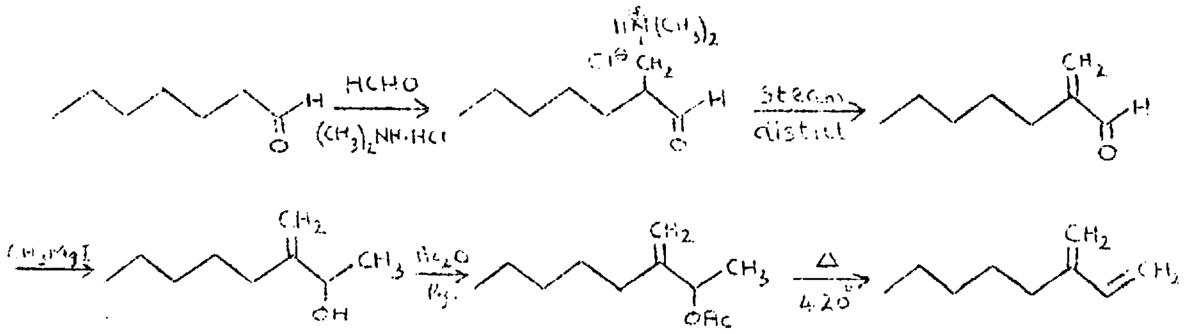
Alternatively, protonation of the π electron system of the diene by acetic acid might bring about a similar re-arrangement, the product being thermodynamically the more stable isomer, due to greater effective substitution. Whatever the mechanism, it is interesting to note that such re-arrangements are possible, and this emphasises the necessity of reducing contact time between the allylic acetate and the 'cracking' surface to a minimum.

3:4:5:6-tetramethylphthalic anhydride is exceedingly resistant to nucleophilic attack due to steric overcrowding (compare 3-isopropyl-4-methylphthalic anhydride). When it is refluxed for three days with 10% aqueous sodium hydroxide, it is converted to a sodium salt. Careful acidification with hydrochloric acid yields free 3:4:5:6-tetramethylphthalic acid, obtained as fine needles. The acid, however, eliminates water at 60° to reform the anhydride, which is also formed when the acid is treated with a cold benzene solution of phosphorus pentachloride. The anhydride is unattacked by fusing with 0.880 ammonia solution, and not surprisingly, the urea melt method failed to cyclise it to a phthalocyanine. Unlike 3-isopropyl-4-methylphthalic anhydride, it is unaffected by prolonged contact with ethanol in dilute solution.

H. General comments on the diene synthesis

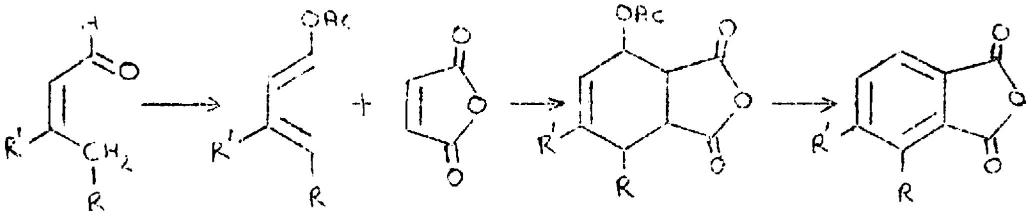
This section of work, though involving some very interesting chemistry has failed except in one case, to produce any new series of substituted phthalocyanines. It would be wrong, however, to conclude that further work along these lines would be fruitless for the indications are all to the contrary. The small sample of what must undoubtedly have been tetrakis-4-isobutylphthalocyanine copper (II) has confirmed that longer chain substituents in the 4-positions of the macrocycle bring about greatly enhanced solubility, and the diene synthesis seems to be the most convenient general route to these compounds. Separation of diene mixtures, or mixtures of their Diels-Alder adducts is the most time consuming process, so it is desirable that methods should be found to reduce the number of side reactions that seem to occur when the dienes are being prepared. Scrupulous purifying of allylic acetates prior to 'cracking', and higher temperatures, larger catalyst surface areas, and much faster flow rates during cracking to reduce contact time, may well bring about great improvements. The ready availability of a large number of methyl alkyl ketones renders the acetylenic alcohol route to allylic acetates quite generally applicable, and where particular ones are not available, alternative routes to substituted phthalic anhydrides exist. Time did not permit any of these alternatives to be studied, but it is worth outlining them here for completeness.

The best of these, as mentioned earlier, seems to be the diene synthesis of Marvel and his co-workers(65) which makes use of long chain aliphatic aldehydes. For example, 2-*n*amylbutadiene may be prepared from *n*-heptaldehyde as follows :

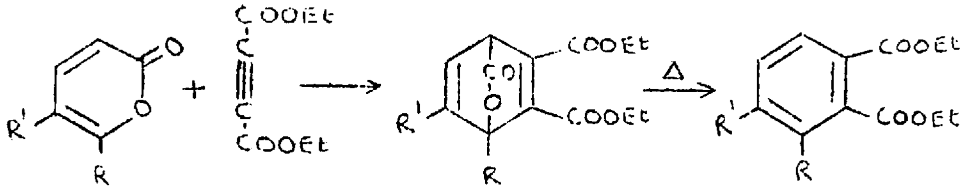


This method depends on the availability of aldehydes.

Blanc(95) condensed the acetates of α:b-unsaturated aldehydes with maleic anhydride, and these adducts could be aromatised to substituted phthalic anhydrides :



Alternatively Shusherina's method may be used, making use of 2-pyrones(96) :



The last two methods introduce groups into the 3-position of the resulting phthalic anhydride, but this does not matter as long as these are methyl groups. Larger groups might introduce undesirable side effects.

There is certainly room for much more work here, but nonetheless, this route to substituted phthalocyanines is of very general applicability.

J. Experimental Section

p-Nitrocumene (96)(98)(99)

A mixture of concentrated sulphuric acid (288g) and concentrated nitric acid (144g) was cooled in an ice/salt bath, and cumene (166ml, 144g) added dropwise with vigorous stirring, such that the temperature did not go outside the limits -1 to +6°, the addition taking 35 minutes. The mixture was stirred for a further hour, poured into 1 litre of distilled water, ether (100ml) added, and the whole shaken vigorously. The aqueous layer was twice washed with ether (100ml) and the ether extracts and product combined and dried over anhydrous potassium carbonate. The preparation was repeated twice more, and the combined products distilled under reduced pressure, p-nitrocumene being collected as a yellow oil, b.p. 110 - 20°/8 mm; yield 303g, 51%

Lit.(80) b.p. 128 - 32°/15mm; yield 530g, 90%.

p-Aminocumene (104)

p-Nitrocumene (50g) was dissolved in ethanol (60ml) and raney nickel W-4 grade(97) (5g) was added. The mixture was poured into a stainless steel autoclave, 200ml capacity (Baskerville and Lindsay Limited, Manchester) and hydrogenated at room temperature over night at 50 lb pressure, being stirred continually. The product was filtered hot through charcoal and distilled under reduced pressure.

Yield 37.5g, 92%; b.p. 110°/26 mm.

This was repeated on the large scale, using p-nitrocumene (425g) but trouble was encountered on stirring, and most of the nitro compound was recovered unchanged.

Preparation of 3-methyl-1-hepten-3-ol (123)(123A)(132)(137)(141)(148)

Since the results of these attempts are listed in table IV, only one run will be described in detail. Magnesium turnings (25g) were suspended in ether (150ml, sodium dried) and a few ml of n-butylbromide added. When the reaction had started, a solution of n-butylbromide (90ml, 144g) in ether (360ml, sodium dried) was added with vigorous stirring at such a rate as to maintain a rapid reflux. The mixture was then stirred under reflux on a water bath until all the magnesium had dissolved (90 min). The flask was cooled in a bath of ethanol and 'Cardice' and a solution of methyl vinyl ketone (62g) in ether (300ml, sodium dried) added dropwise with vigorous stirring, such that the temperature did not go outside the limits -34 to -31°. When about 90% of the ketone had been added, yellow clouds were observed as each drop entered the reaction mixture, indicating a major side reaction; so at this point addition was ceased. The mixture was stirred overnight and worked up with a solution of ammonium chloride (60g) in water (150ml). After standing for six hours, the ether layer was decanted off, the white pasty residue being extracted with ether (3 x 150ml) and the extracts dried over anhydrous magnesium sulphate. Fractional distillation yielded a sample, 15g, b.p. 64°/27 mm, containing the allylic alcohol, and a ketone. The ketone was identified by the preparation of its semicarbazone and 2:4-dinitrophenyl hydrazone :

2-octanonesemicarbazone	m.p. 123°	Found	124°
2-octanone-2:4-D.N.P.	m.p. 58°	Found	59°.

Further fractional distillation failed to separate the alcohol and ketone.

<u>3:5-Dimethyl-1-hexyn-3-ol (120)(122)(143)</u>

Sodium (50g) was dissolved in liquid ammonia (1500ml) after the addition of ferric nitrate (0.5g), and the solution stirred until it had become grey (3 hrs). A rapid stream of acetylene was passed into the resulting suspension of sodamide until it had become very dark grey (2 hrs), the reaction mixture being topped up with liquid ammonia from time to time. A solution of methyl*iso*butyl ketone (250ml, 200g) in ether (250ml, sodium dried) was added with vigorous stirring over 40 minutes, and the resulting product stirred for three hours. It was worked up by the cautious addition of solid ammonium chloride (120g), and the ammonia allowed to evaporate. The product was extracted with ether, the ether extracts being dried over anhydrous sodium sulphate (1 hr) and then ahydrous potassium carbonate. Fractional distillation at reduced pressure yielded 172g, 68%. A small sample was redistilled at atmospheric pressure.

B.p. 148°/755 mm; n_D^{20} 1.4345.
Lit.(98) b.p. 148°/760 mm; n_D^{20} 1.4360.
Calc. for $C_8H_{14}O$:
C = 76.14, H = 11.18
Found : C = 75.80, H = 11.10 %

3-Acetoxy-3:5-dimethyl-1-hexyne (144)

The acetylenic alcohol (6.5g) was mixed with acetic anhydride (20g) and pyridine (0.1g), the mixture being heated on a steam bath for 18 hours. It was poured into cold water, shaken vigorously, ether (50ml) added, and the water layer discarded. The ether layer was shaken with portions of aqueous sodium carbonate until evolution of carbon dioxide had ceased, then with water, and dried over anhydrous calcium chloride. It was distilled under reduced pressure. A sample, b.p. 46-7°/0.25mm; n_D^{20} 1.4305 was analysed.

$C_{10}H_{16}O_2$ requires :

C = 71.39, H = 9.58, O = 19.03

Found : C = 71.25, H = 9.65, O = 18.84 %

3:5-Dimethyl-1-hexen-3-ol (121)(125)(145)

A typical run is described. The acetylenic alcohol (158g) was dissolved in ethanol (750ml) and catalyst (2.0g, palladium on strontium carbonate, Johnson Matthey and Company Limited) added. The mixture was shaken under a slight positive pressure in an atmosphere of hydrogen at 23°, until the theoretical quantity of gas had been taken up (approx. 30.5 litres). The solution was filtered, the ethanol removed at atmospheric pressure, the product distilled. Yield 120g, 75%. Analytical fraction b.p. 145.5°/763mm; n_D^{25} 1.4314.

Lit.(99) b.p. 146-7°/760mm; n_D^{20} 1.4342.

Calc. for $C_8H_{16}O$:

C = 74.94, H = 12.58, O = 12.48

Found : C = 74.78, H = 12.42, O = 12.45

1-Acetoxy-3:5-dimethyl-2-hexene (129)

3:5-Dimethyl-1-hexen-3-ol (3g) was heated on a steam bath with acetic anhydride (15ml) for three days. The product was diluted with ether (20ml), shaken with portions of aqueous sodium carbonate (10%), washed with water, and dried over calcium chloride.

Distillation gave a constant boiling fraction 161°/757 mm, identified by its N.M.R. spectrum as 1-acetoxy-3:5-dimethyl-2-hexene.

3-Acetoxy-3:5-dimethyl-1-hexene (138)(146)

3:5-Dimethyl-1-hexen-3-ol (471g) was mixed with acetic anhydride (1400ml), and pyridine (3ml), and the mixture was heated on a steam bath at 96° for 40 hours. It was poured into water (2 litres), stirred for 1 hour and ether (500ml) added. The ether layer was washed with aqueous sodium carbonate until there was no further evolution of carbon dioxide, and then dried over calcium chloride. It was distilled under reduced pressure, the fraction b.p. 44-56°/0.55 mm being collected.

Dehydration of 3:5-dimethyl-1-hexen-3-ol (133)

The alcohol was distilled at atmospheric pressure into a heated tube (290-320°) packed with 20% zirconia supported on pumice, at such a rate that the distillate was collected at about sixty drops per minute, and the temperature at the still head was maintained between 90 - 100°. The catalyst was kindly prepared by Dr. A.J.E. Welch of this department, by igniting pumice, previously soaked in a concentrated solution of zironylnitrate. Activation was completed by passing a slow stream of air through the catalyst for 24 hours, heated at 350°. The product was fractionated, the fraction boiling between 117 - 47° being recycled. In all, 37ml of water was collected, and much sweet smelling gas was lost. Refractionation gave 165g of product, boiling in the range 77 - 117°, and this was redistilled at atmospheric pressure, using a column of 25 plate efficiency. A fraction boiling 69 - 106°/757 mm was shown by V.P.C. to contain five components, and a second fraction boiling between 106.7 - 109.1°/758 mm was similarly shown to contain three components, including methyl _iso_butyl ketone. A constant boiling fraction (108°/760 mm) contained both diene and ketone. Examination of the residue in the still pot yielded a syrupy polymer. This was dissolved several times in benzene, on each occasion being reprecipitated by pouring into an excess of ether, and was finally heated under vacuum for two days (100°/0.03 mm). The polymer was of the consistency of pitch at room temperature, and pale brown in colour.

$(C_8H_{14})_n$ requires :

$C = 87.19, \quad H = 12.81.$

Found : $C = 87.32, \quad H = 12.86$ %

M.W. 1480, corresponding to 13 - 14 units per chain.

3:5-Dimethyl-1:3-Hexadiene (146A)

During the vacuum distillation of 3-acetoxy-3:5-dimethyl-1-hexene, the liquid nitrogen trap of the vacuum pump became clogged. The liquid isolated from the trap was stirred with anhydrous sodium carbonate and distilled under reduced pressure, the fraction boiling 24 - 6°/27 mm being collected. A small sample was refractionated, the fraction b.p. 111.5 - 112°/774 mm, n_D^{20} 1.4426 being analysed.

C_8H_{14} requires :

$C = 87.19, \quad H = 12.81$

Found : $C = 86.28, \quad H = 12.88$ %

The N.M.R. spectrum showed it to be a mixture, and the infra red showed ketone to be present.

3-Isopropyl-4-methyl-1:2:3:6-tetrahydrophthalic anhydride (147)

Maleic anhydride (20g) was dissolved in benzene (100ml) and picric acid (20mg) added. Diene mixture (27g) was added, and when the reaction had ceased, the product was refluxed for 16 hours. It was filtered hot through charcoal, evaporated down to about 30ml and recrystallised from petroleum ether (60-80°). Sublimation at $90^{\circ}/10^{-2}$mm left a brown residue, which on resublimation at $40^{\circ}/2 \times 10^{-5}$mm yielded white plates. Some of these were recrystallised from petroleum ether (80-100°), m.p. 140.5 - 141.5°.

$C_{12}H_{16}O_3$ requires :

$C = 69.18, \quad H = 7.75, \quad O = 23.07$

Found : $C = 69.00, \quad H = 7.38, \quad O = 23.09$ %

3-Isopropyl-4-methylphthalic anhydride (150)

The tetrahydro anhydride (14g) was dissolved in hot glacial acetic acid (28ml), and a solution of bromine (15g) in acetic acid (45ml) was added dropwise over 40 minutes. The whole was refluxed for 16 hours, the acetic acid pumped off under reduced pressure, and the tarry residue heated at 200° for seven hours. The product was extracted with boiling petroleum ether

(80-100°), stirred with a few ml. of acetone to remove some yellow gum, and recrystallised from acetone.

Yield 3.0g, m.p. 176.5 - 177°.

$C_{12}H_{12}O_3$ requires :

C = 70.55, H = 5.95, O = 23.50

Found : C = 70.62, H = 5.91, O = 23.47 %

3-*Iso*propyl-4-methylphthalimide (151)

The anhydride (2.25g) was mixed to a slurry with 0.880 ammonia solution (5ml) and the semi-solid mass heated slowly on a Wood's metal bath. Most of the water came off below 150°, and the product fused at 270°. It was sublimed twice at 120°/10^{-2}mm.

Yield 2.0g, m.p. 202.5 - 3.5°.

$C_{12}H_{13}NO_2$ requires :

C = 70.92, H = 6.45, N = 6.89, O = 15.74

Found : C = 71.03, H = 6.20, N = 7.06, O = 15.63 %

Reaction with ammonia solution (152)

3-*Iso*propyl-4-methylphthalimide (1.8g) was finely ground and stirred vigorously with 0.880 ammonia solution (7ml) for 24 hours. The product was filtered off, and was found to be starting material (100% recovery).

Reaction with sulphuric acid and methanol (154)

3-*Iso*propyl-4-methylphthalimide (1.8g) was dissolved in methanol (50ml), concentrated sulphuric acid (1.5ml) added, and the solution heated under reflux for 18 hours. The product was poured into water (250ml), the white solid filtered off, and dried in vacuo at room temperature.

Yield 1.5g unchanged imide.

Attempt to cyclise the imide (157)

3-Isopropyl-4-methylphthalimide (1.45g) was mixed in the urea (1.45g), anhydrous copper sulphate (0.35g), molybdenum oxide (4mg) and chlorobenzene (0.52g), and the whole stirred into 1:2:4-trichlorobenzene (6.0g). The mixture was heated on a Wood's metal bath, the temperature slowly rising to 180°, and being maintained at this value for six hours. No pigment was isolated.

Pyrolysis of 3-acetoxy-3:5-dimethyl-1-hexene (165)

The allylic acetate was added at the rate of 20 drops/minute to the top of a silica tube, packed with glass beads (0.3 cm), and heated to 500°, in a stream of nitrogen gas. The issuing gases were condensed in a receiver immersed in crushed 'Cardice' and worked up in much the same way as has been described in the preparation of 1:3-pentadiene. Distillation of the product yielded a fraction boiling between 64 - 72°/190 mm, and this was refractionated, samples boiling between 110 - 14°/761 mm being collected.

Yield 81g from 177g acetate, 70%

A sample, b.p. 109 - 10°/765 mm, n_D^{23} 1.4348, was submitted for N.M.R. studies, and microanalysis.

C_8H_{14} requires :

$C = 87.19, \quad H = 12.81$

Found : $C = 86.10, \quad H = 12.98$ %

The sample was shown to contain diene(s), some acetylenic derivative, and a trace of ketone.

Diels-Alder adducts (166)

(i) Diene fraction b.p. 106 - 113° (36g, 51ml) was added to a solution of maleic anhydride (33g) in benzene (125 ml), and a trace of picric acid. It was refluxed for 16 hours, and worked up in the usual fashion. Yield 61g, low melting oily solid. One recrystallisation from petroleum ether (60 - 80°) yielded 30g of yellow oil, and 28.5g white solid.

(ii) This was repeated, using diene fraction b.p. 113 - 4° (18.5g, 25.6ml) and maleic anhydride (16.5g), to give 34g adduct. Recrystallisation from petroleum ether (80 - 100°) yielded 10g yellow oil, and 18.5g white solid. A sample of the white solid was recrystallised to constant melting point from petroleum ether (80 - 100°), m.p. 78 - 9°.

$C_{12}H_{16}O_3$ requires :

$C = 69.18, \quad H = 7.75, \quad O = 23.07$

Found : $C = 69.55, \quad H = 7.68, \quad O = 22.95$ %

The N.M.R. spectrum showed that this was a mixture of two isomeric adducts.

(iii) Diene fraction b.p.110 - 113° (12.5g, 16.8ml) was reacted with maleic anhydride (110g). Yield 21g yellow oil, from which a little white solid could be separated.

Oxidative bromination of solid adduct (168)

The solid adduct (57.5g) was dissolved in glacial acetic acid (120ml), and oxidised in the usual manner with a solution of bromine (180g) in acetic acid (180ml). The product was taken up in boiling acetone (400ml), filtered twice through charcoal, and evaporated down until no more acetone came off. The semi-solid brown residue was stirred with acetone (150ml) and filtered, 3-isopropyl-4-methylphthalicanhydride (8g) being isolated. The residue was heated overnight with aqueous sodium hydroxide on a steam bath, cooled, and extracted three times with ether to yield a further 10g of 3-isopropyl-4-methylphthalic anhydride. The aqueous solution was acidified with concentrated hydrochloric acid, extracted with ether, and the isolated brown oil taken up in acetone, charcoaled and dried over calcium chloride. The product after removal of acetone was slowly heated under reduced pressure to 250°, during which time 10ml of water was eliminated, and was finally isolated as a low melting syrupy oil. Attempts to crystallise this product were without success. It was believed to be impure 4-isobutylphthalicanhydride.

Attempt to cyclide 4-*iso*butylphthalicanhydride (197)

The syrupy anhydride from above (2g) was mixed with urea (2g), cuprous chloride (0.32g), ammonium molybdate (20mg) and chlorobenzene (0.6ml). This was added with stirring to 1:2:4-trichlorobenzene (5.5ml), and slowly heated on an oil bath. After 30 minutes, the melt had reached 180°, was homogeneous, and had turned from greenish brown to reddish brown. The melt became dark as the temperature approached 200°, and was maintained here for 90 minutes. The product was crushed, filtered under suction, and the trichlorobenzene solution added to the top of an alumina column. The column was eluted with benzene, and yielded a few milligrammes of a blue solid, believed to be tetrakis-4-*iso*butylphthalocyanine copper(II).

Preparation of phthalocyanine copper(II) (182)

Phthalicanhydride (5.5g), urea (7.5g), cuprous chloride (1.2g) ammonium molybdate (0.4g) and chlorobenzene (3ml) were ground together, and added to 1:2:4-trichlorobenzene (20ml). The flask was heated to 195° over 25min., and maintained at this temperature for 90 minutes. The product was filtered off, washed with acetone, refluxed overnight with aqueous ammonium chloride (10g/100ml), washed with water, then acetone, and dried.

Yield 4.25g, 79.5%.

Oxidative bromination of syrupy adduct (177)

The syrupy maleic anhydride adduct previously described (39.5g) was dissolved in glacial acetic acid (100ml), and oxidised in the usual manner with bromine (122g) dissolved in acetic acid (110ml). The black tarry product was taken up in boiling acetone (1000ml), filtered through charcoal, evaporated down to 50ml and filtered. The brown solid residue was only slightly soluble in acetone, but the filtrate on work up, yielded a quantity of 3-*iso*propyl-4-methylphthalic anhydride. The brown solid residue was sublimed ($120^{\circ}/10^{-6}$mm) and yielded 7g white needles, m.p. 276 - 8° after two recrystallisations from acetone. Lit.$^{(93)}$ 260°.

Calc. for $C_{12}H_{12}O_3$:

C=70.55, H = 5.95, O = 23.50

Found : C=70.31, H = 5.71, O = 23.25 %

3:4-Dimethylhexane-3:4-diol (187)

This was prepared in a similar fashion to the preparation of pinacol, described in Chapter 4. Methylethyl ketone (618ml 498g) was reduced by magnesium turnings (80g) and mercuric chloride (90g) in anhydrous benzene (1000ml). When the reaction had subsided, the mixture was heated on a steam bath for 2 hours, with periodic shaking, benzene (610ml) being added to loosen the syrupy mass. The product was worked up with water (200ml), the solid being broken up with a rod, and then filtered. The solid was leached with benzene (800ml) on a steam bath for 3 hours, and the benzene extracts combined and distilled on a steam bath. When no more benzene and water came off, the oily product was distilled under reduced pressure. Yield 430ml, b.p. 99 - 120°/22 mm. This was used in a crude form for the next stage.

Dehydration of the diol (188)(189)

(i) 3:4-Dimethylhexane-3:4-diol (430ml) was mixed with acetic anhydride (1750ml) and phosphoric acid (25ml), and heated slowly on a mantle. The contents of the flask had reached 120° after one hour, and at 130°, gentle boiling began. The temperature settled at 133 - 4°, liquid distilling over at 90°, and the main fraction being collected at 120 - 4°/754 mm. Distillation was continued until all the acetic acid and acetic anhydride had come off, the temperature of the still pot having risen to 310°. The distillate proved to be acetic acid, acetic anhydride, and some allylic acetate. No diene was isolated.

(ii) 45% Hydrobromic acid (8ml) was added to the diol (330g), and the mixture slowly heated. Water and an organic liquid came over at 91°/760mm, the distillation being continued for 3½ hours until 192ml crude organic layer and 62ml water had been collected. The organic layer was washed with water, dried over calcium chloride and distilled at 760mm.

Yield :		
	114 - 22°	40g
	122 - 30°	21g
	130 - 35°	45g

The lower boiling fraction contained predominantly 3:4-dimethyl-cis.trans-2:4-hexadiene, and the higher boiling fraction 3:4-dimethyl-trans.trans-2:4-hexadiene. The midfraction was a mixture.

3:4:5:6-Tetramethyl-1:2:3:6-tetrahydrophthalicanhydride (191)

3:4-Dimethyl-trans.trans-2:4-hexadiene (45g) was added to a solution of maleic anhydride (36g) in benzene (200ml). The reaction was extremely vigorous, there being no induction period. The product was refluxed for 48 hours, evaporated to dryness, taken up in acetone and filtered hot through charcoal.
Yield 74g crude.

A sample was recrystallised three times from petroleum ether (80 - 100°), m.p. 114°. Lit.(93) 113-4°. Yield 71g, 87.5%.

Calc. for $C_{12}H_{16}O_3$:

$C = 69.18$, $H = 7.75$, $O = 23.07$

Found : $C = 70.41$, $H = 7.80$, $O = 22.70$ %

3:4:5:6-Tetramethylphthalicanhydride (194)

The adduct from above (70g) was dissolved in glacial acetic acid (145ml) and oxidised in the usual manner with bromine (220g) in acetic acid (220ml). After work up, a white solid was isolated, sublimed at $120^\circ/10^{-6}$mm and recrystallised from acetone, m.p. 276°.

Calc. for $C_{12}H_{12}O_3$:

$C = 70.55$, $H = 5.95$

Found : $C = 70.33$, $H = 5.81$ %

3:4:5:6-Tetramethylphthalicacid (186)

The anhydride (0.5g) was refluxed for three days with 10% aqueous sodium hydroxide (25ml). The solution was filtered through asbestos wool, cooled to 0° and concentrated hydrochloric acid added until the solution was acid. The white aqueous suspension was extracted with two portions of ether (2 x 50ml), the ether extracts dried (magnesium sulphate) and evaporated to dryness at room temperature. The white needles eliminated water at 60° to give the anhydride.

Calc. for $C_{12}H_{14}O_4$:

C = 64.85, H = 6.35, O = 28.80

Found : C = 65.24, H = 6.35, O = 28.02 %

Action of phosphorus pentachloride (190)

3:4:5:6-Tetramethylphthalicacid (0.25g) was added to a cold solution of phosphoruspentachloride (0.5g) in benzene (15ml, sodium dried), the mixture shaken and allowed to stand at room temperature for three hours. It was then warmed to just below its boiling point, filtered hot and cooled. Crystals of the anhydride were deposited, but no acid chloride was detected.

Action of ammonia on the anhydride (184)

The anhydride (1.5g) was slurried with 0.880 ammonia solution (5ml) and heated over two hours to 300°. The product was crushed and sublimed (130°, 10^{-5}mm). The infra red spectrum showed it to be unchanged anhydride, no imide being detected.

CHAPTER 8

SOME NUCLEAR MAGNETIC RESONANCE STUDIES

A. Introduction

During the past five years, much work has been done on the N.M.R. spectra of the porphyrins, and the related chlorins.. Spectra are recorded of a large number of ring substituted, and metal derivatives(100)(101)(102)(103)(104)(105) in solvents such as deuterochloroform, trifluoroacetic acid and deuterotrifluoroacetic acid; and shifts in the position of bands have been noted with changes in concentration(106). In these compounds, the N-H protons in the centre of the ring appear at 14 to 15τ, and the peripheral protons at -1 to 0τ, the large shifts being attributed to the ring current of the eighteen electron aromatic system. Phthalocyanines contain a similar eighteen electron system, which is also believed to be aromatic; but unlike the porphyrins, the phthalocyanines are exceedingly insoluble, and present something of a challenge to the N.M.R. spectroscopist. A systematic study of the N.M.R. properties of the phthalocyanine ring would involve obtaining information about the shielding effect of the large aromatic nucleus upon the central two hydrogen atoms, and the relative deshielding effects upon the hydrogen atoms in the 3 and 6 , and the 4 and 5 positions. The effect of substitution upon the line positions and form would also be useful. Becker(107) prepared a solution of phthalocyanine in

100% deuterosulphuric acid, and observed a broad doublet (half width, about 15 cps), at 0.41 and 1.48τ. The pigment was almost certainly in solution as the di-cation, and so these bands will be to lower field of the true band positions of phthalocyanine. No information was obtained about the N-H protons, since these would exchange with the solvent, and would not appear. The only practical way of obtaining measurements on these latter, would be to synthesise a phthalocyanine with sufficiently long alkyl side chains in the 4-positions, to render it soluble in solvents such as chloroform and carbon tetrachloride. No attempt was made in this work to do this. Information about the ring protons could only be obtained if the phthalocyanine were to be solublised without making use of ring substitution, and this could be attempted in two different ways. Long chain alkyl or alkoxy groups could be attached to the metal atoms of a phthalocyanine containing a diamagnetic metal with valency greater than two. Ideal models could be obtained by extending some of the work done by Kenney and his co-workers on derivatives of aluminium, silicon, germanium(IV) and tin(IV)(108)(109)(110)(111). The other method would be to render a paramagnetic divalent metal phthalocyanine diamagnetic by co-ordination of suitable groups on to the metal from above and below the plane of the ring. The ideal model for these studies is phthalocyanine iron(II) and its dicyano complex, and it was earlier work carried out by Lever in this department(52) which led to the results to be described in this chapter. Dipotassium [phthalocyanine dicyanoferrate(II)] together with its tetrakis-3-methyl and tetrakis-4-methyl derivatives have been prepared, and their N.M.R. spectra are recorded in methanolic potassium cyanide solution. Before discussing these, however, it is useful to comment on the spectra of some substituted phthalic anhydrides, which show the effects of methyl substitution upon line positions. All spectra recorded here, and elsewhere in this thesis, were run on a 'Varian A60' 60 Mc spectrometer; measurements being made from an internal reference of tetramethyl silane. The calibration of the instrument was checked.

B. Substituted phthalic anhydrides

The N.M.R. spectra of phthalic anhydride, and four of its derivatives are listed in Table V. Substituents in the 3, 4, 5 and 6 positions are tabulated, together with τ values.

Table V

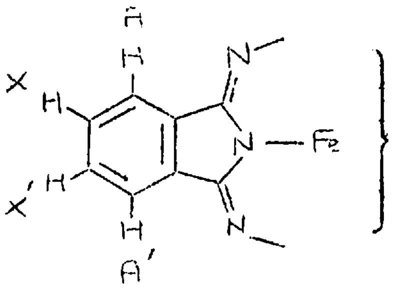
Position	Phthalic Anhydride (P.A.)		3-Methyl- P.A.		4-Methyl- P.A.		4:5-dimethyl- P.A.		3:4:5:6-tetramethyl P.A.	
3	H	2.02	CH_3	7.25	H	2.14	H	2.22	CH_3	7.37
4	H	2.02	H	-	CH_3	7.38	CH_3	7.50	CH_3	7.65
5	H	2.02	H	-	H	2.25	CH_3	7.50	CH_3	7.65
6	H	2.02	H	-	H	2.08	H	2.22	CH_3	7.37

Treatment of the spectrum of phthalic anhydride as an A_4 system is not strictly accurate, as there is slight splitting of the single line. This is, however, exceedingly small. The aromatic protons of 3-methylphthalic anhydride form an ABC system, and values for the line positions were not extracted. The aromatic protons of 4-methylphthalic anhydride were treated as an AMX system, in which JAX = 0. This again is not strictly accurate, as the para-splitting is probably not quite zero. The results, in Table V, show that substituents in the 3 and 6 positions are at lower field than corresponding substituents in the 4 and 5 positions, due to greater deshielding by the anhydride ring. Also, the introduction of methyl groups shifts all the lines to higher field. The deshielding effect of the phthalocyanine ring should be very much greater than that of the anhydride, in view of its aromaticity and larger diameter. Hence the proton resonance lines should be at lower field. Another effect on the spectra of phthalocyanines should be a large chemical shift between the 3, 6 and 4, 5 pairs of protons. This is observed.

C. Dipotassium [Phthalocyaninedicyanoferrate(II)]

This was prepared by a method identical to that of Lever(52). Phthalocyanine dipyridine iron(II) was sublimed at 400°/10^{-6}mm, and the resulting phthalocyanine iron(II) dissolved in boiling methanolic potassium cyanide. The solution was filtered, evaporated to dryness, and a 40mg sample taken up in methanol containing a little potassium cyanide (0.6ml) to give the solution on which measurements were made.

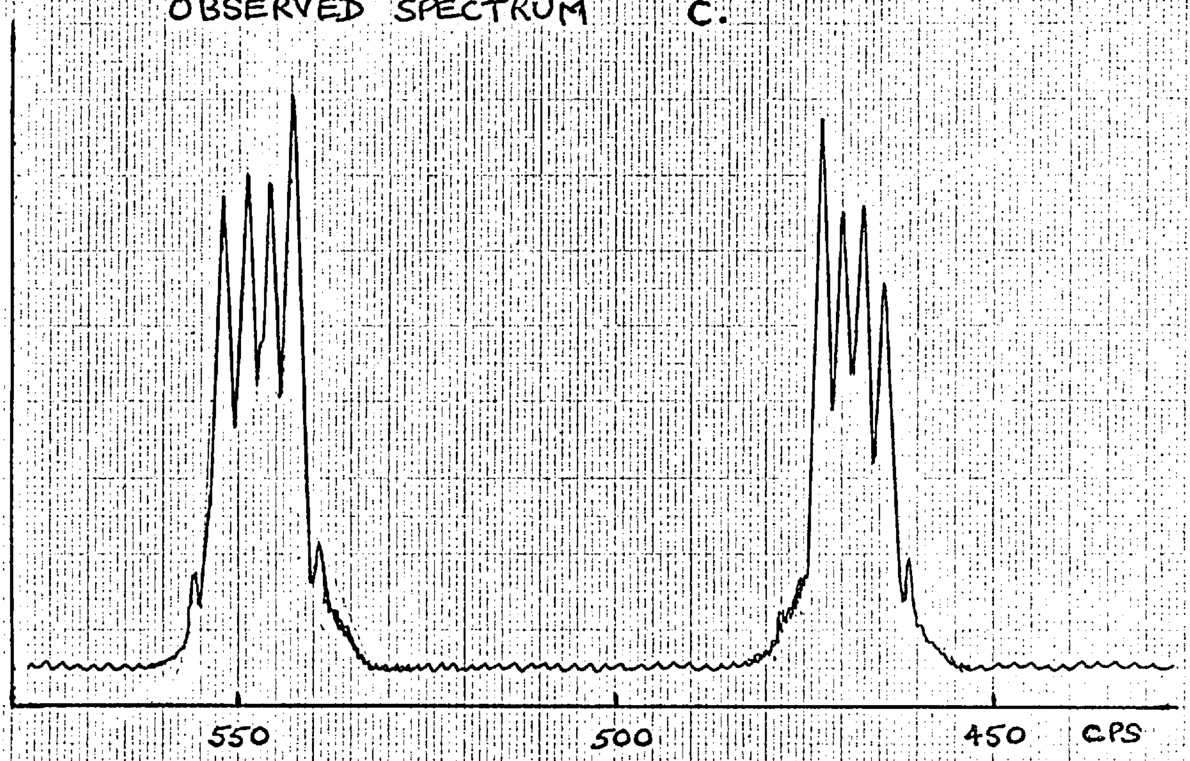
At first sight the spectrum appeared to be made up of two symmetrical quartets, with origin positions at 0.88τ and 2.18τ, corresponding respectively to the 3 and 6 and to the 4 and 5 protons. Closer examination, however, revealed at least six lines in each group, so the system was treated as an A_2X_2 case,

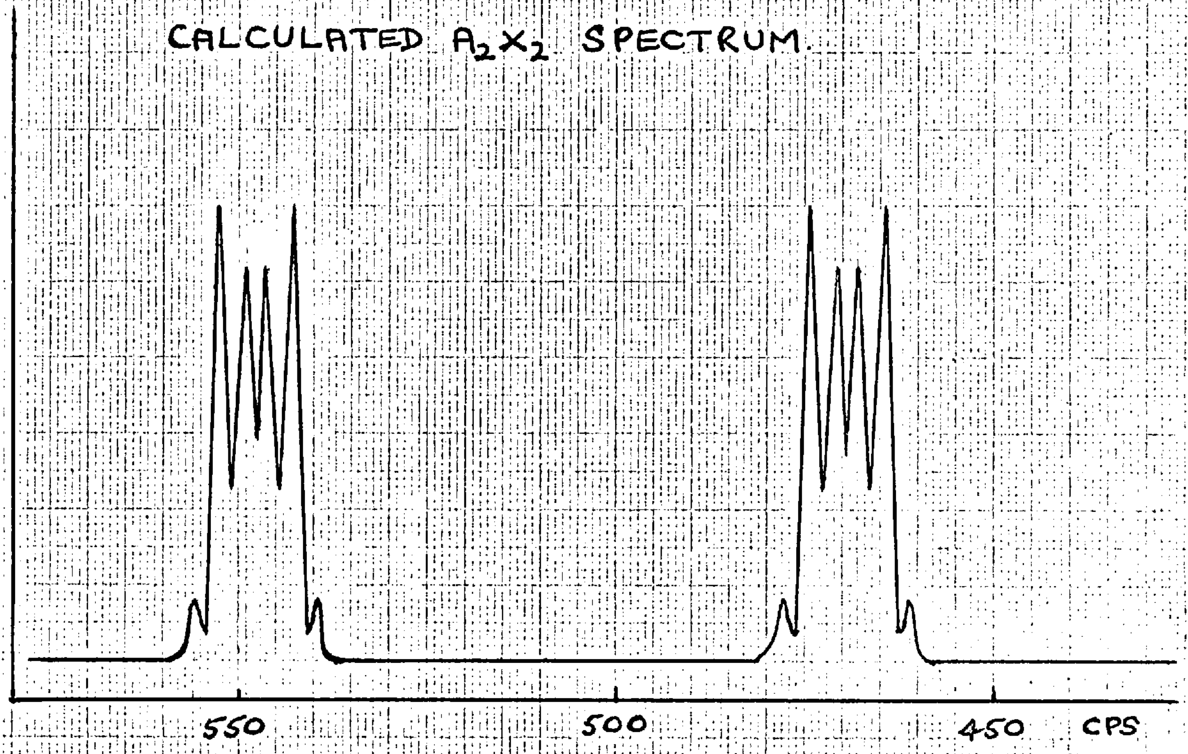


The theoretical A_2X_2 spectrum contains two sets, each of twelve lines, corresponding to the A part and the X part, these being brought about by interactions between the A and X, A and X', A and A' and X and X' protons. By making suitable measurements on the line positions and separations, it was possible to calculate the positions of all twentyfour lines, and hence to obtain the coupling constants of the system. These data are listed below, and are illustrated in Fig.I.

As expected, ν_A and ν_X are at higher field than the positions observed by Becker for phthalocyanine in deuterosulphuric acid, and the chemical shift is larger. The size of this chemical shift (1.31 p.p.m.) is a measure of the deshielding effect, and

FIG. I


OBSERVED SPECTRUM C.


CALCULATED A_2X_2 SPECTRUM.

hence of the aromaticity of the phthalocyanine nucleus. Although the 3 and 6 protons are shifted quite a way to low field, the 4 and 5 protons are in much the same position as in phthalic anhydride, showing that the deshielding effect of the phthalocyanine ring has quite a limited range.

$\nu_A = \nu_{A'} = 547.6$ cps, 0.87τ

$\nu_X = \nu_{X'} = 469.2$ cps, 2.18τ

$\delta_{AX} = 78.4$ cps, 1.31 p.p.m.

$J_{AX} = J_{A'X'} = 7.80$cps

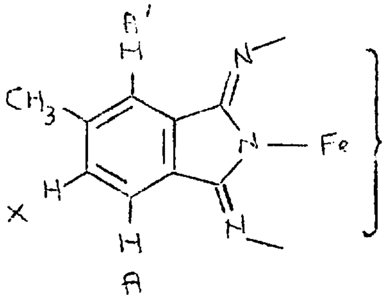
$J_{XX'} = 7.00$cps

$J_{AX'} = J_{A'X} = 1.20$ cps

$J_{AA'} = 0.40$ cps

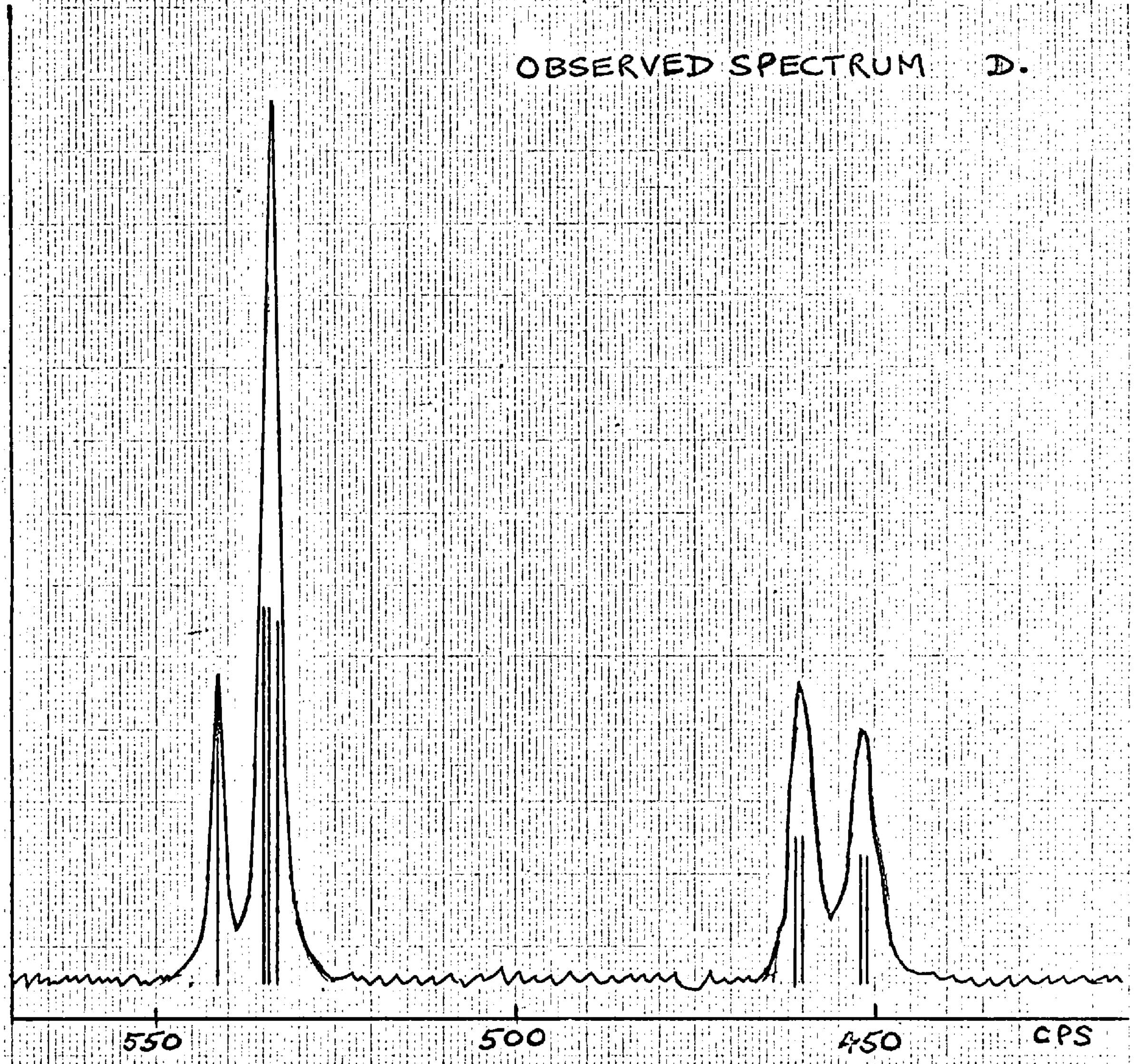
D. Dipotassium [tetrakis-4-methylphthalocyaninedicyanoferrate(II)]

The preparation of the solution of this compound is described in Chapter 3.



The spectrum (Fig.II) shows two doublets in the aromatic region, the low field doublet (A proton) having superimposed upon it a singlet (A' proton). There is slight broadening of the high field doublet (X proton) due to meta coupling with the A' proton, and although no splitting is observed, an approximate

FIG. II



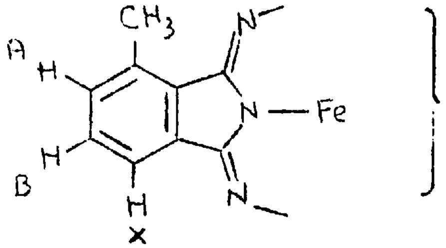
value of the meta coupling constant can be estimated from the half width of the lines. Para coupling was taken to be negligible, and the parameters were extracted on a first order basis.

ν_A = 537.0 cps, 1.05τ
$\nu_{A'}$ = 534.1 cps, 1.10τ
ν_X = 457.6 cps, 2.37τ
ν (CH_3) = 170.5 cps, 7.16τ
δ_{AX} = 79.8 cps, 1.33 p.p.m
J_{AX} = 8.40cps,
$J_{A'X}$ = 1.0 cps

Once again the 3 and 6 protons are shifted to low field due to the deshielding effect of the phthalocyanine ring, but this time this is overcome to a certain extent by the positive inductive effect of the methyl group. The methyl group is itself shifted to low field rather more than would be expected in view of the results obtained from section C, and this is difficult to explain. Although δ_{AX} remains much the same as for the last compound discussed, J_{AX} has increased quite appreciably.

E. Dipotassium [tetrakis-3-methylphthalocyaninedicyanoferrate(II)]

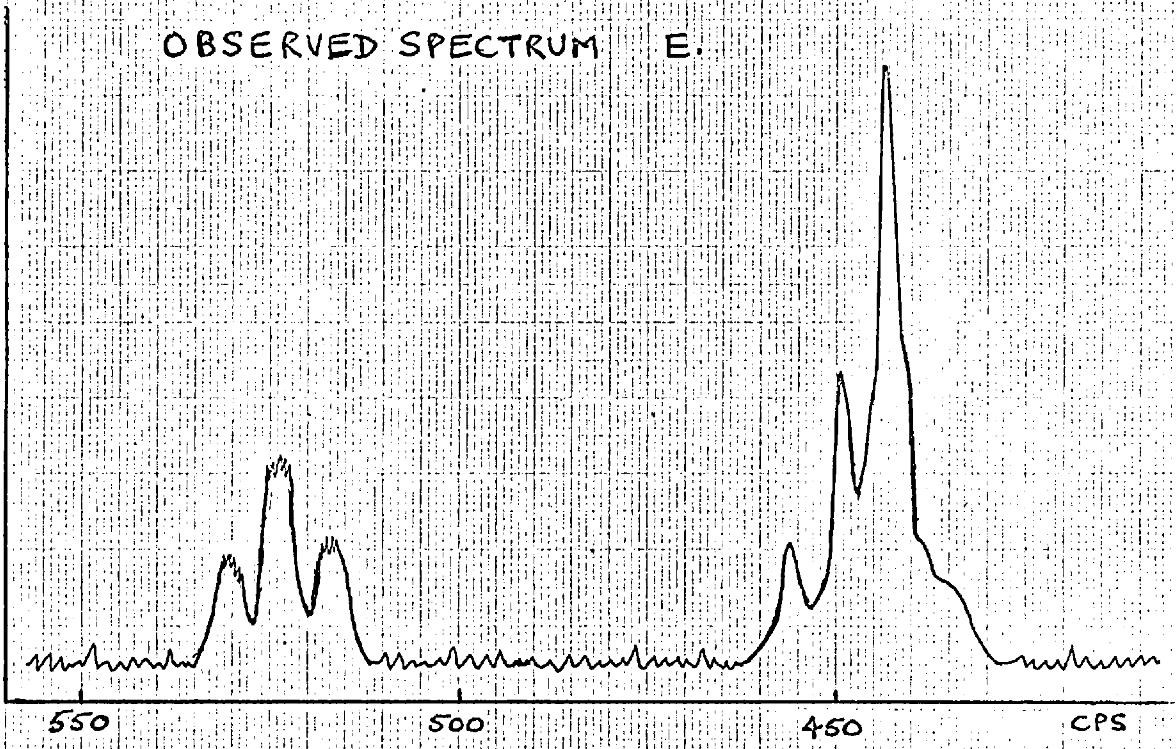
The spectrum of this compound was rather more difficult to interpret, since it was of the ABX form. Only a small amount of the solublised phthalocyanine was available, and the necessarily high amplification resulted in a large amount of background 'noise', which drowned some of the smaller peaks. It was necessary to know the positions of these peaks in order to find line origin positions and coupling constants, so a method of successive approximations was employed, making use of parameters found under sections C and D.



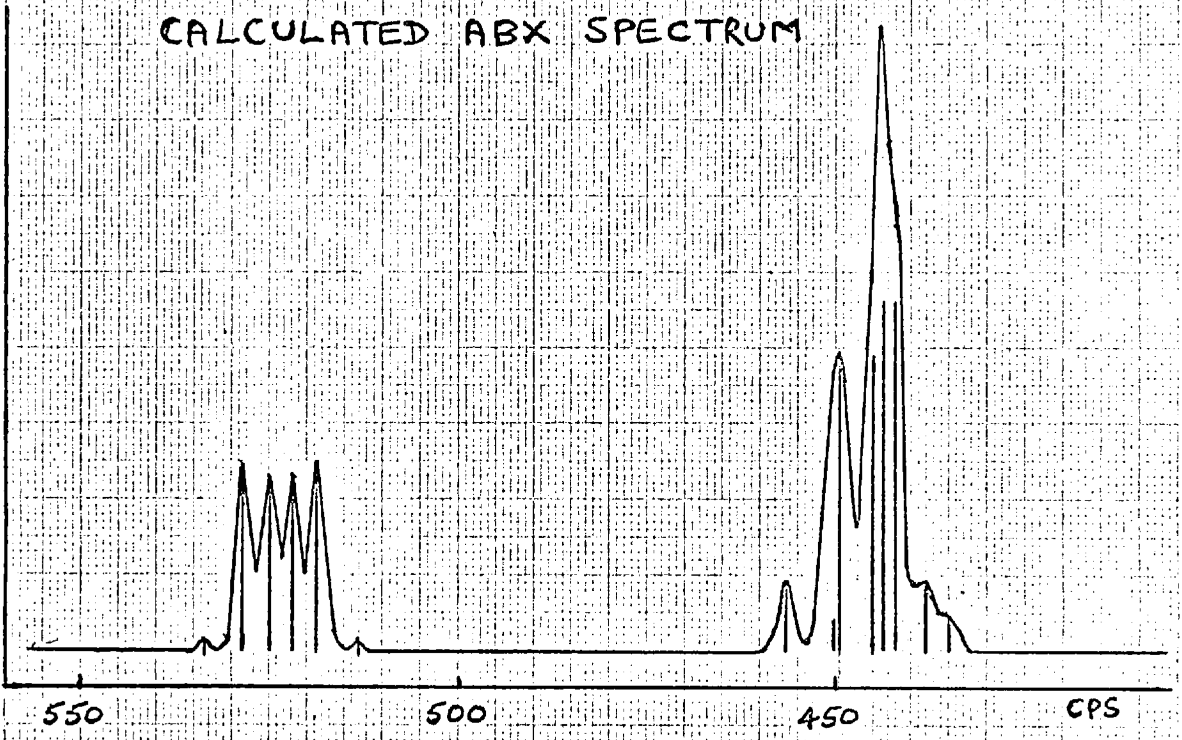
The X proton appeared as a triplet (quartet?) (Fig.III) consisting of three rather broad lines, the origin position being at 1.08τ. The AB protons appeared basically as an unsymmetrical triplet, the intensities being roughly 6:3:1 towards low field. The theoretical ABX spectrum contains fourteen lines, a symmetrical sextet in the X portion and two symmetrical quartets in the AB portion, so attempts were made to locate these latter two quartets. A theoretical 'envelope' was finally constructed which fitted the observed AB pattern exceptionally well, but no series of calculated parameters would fit both the AB and the X portions simultaneously. The values listed below seem to be the best compromise, and both the resulting theoretical spectrum, and the observed spectrum are illustrated in Fig.III.

These figures, none the less, fit in exceptionally well with those obtained in sections C and D. The 6 proton has been shifted to low field as expected, and the 4 and 5 protons to

FIG. III



OBSERVED SPECTRUM E.



CALCULATED ABX SPECTRUM

slightly higher field than was observed in dipotassium [phthalocyaninedicyanoferrate(II)] due to the inductive effect of the methyl group. These latter do, however, seem to be unaffected by the deshielding effect of the phthalocyanine ring. The methyl group itself appears 39 cps (0.65 p.p.m.) to the low field side of that in dipotassium [tetrakis-4-methylphthalocyanine-dicyanoferrate(II)], which is about half the shift observed between the 3 and 4 protons, and is thus much larger than expected. The reason for this is probably that the 3-methyl group is sufficiently close to the neighbouring o-phenylene ring to experience the deshielding effect of this in addition to that of its own ring and of the phthalocyanine nucleus.

ν_A = 452.6 cps, 2.46τ
ν_B = 459.6 cps, 2.34τ
ν_X = 535.6 cps, 1.08τ
$\nu\ (CH_3)$ = 209.4 cps, 6.51τ
δ_{BX} = 76.0 cps. 1.27 p.p.m
J_{AX} = 2.23cps.
J_{BX} = 6.77cps.
J_{AB} 7.30cps.

F. Summary of N.M.R. spectra

The aromatic nature of the phthalocyanine ring has been confirmed by the shift of the 3 and 6 proton lines to low field.

The range of this deshielding effect does not, however, extend to the protons in the 4 and 5 positions, as these give resonance lines in the position usually observed for 1:2-disubstituted benzenes. As predicted from the spectra of substituted phthalic anhydrides, the introduction of methyl groups has shifted the lines of the aromatic protons to higher field by about 12 cps, i.e. 0.2p.p.m. The lines from methyl groups in both the 3 and 4 positions appear at lower field than would be predicted, and although this can be explained in terms of reinforced deshielding in the case of the former, there is no obvious explanation for the latter.

Strictly speaking, the aromatic protons in these dicyano-ferrous complexes will have smaller chemical shifts (measured from T.M.S.) than protons in other metal phthalocyanines. This is because the double negative charge on the cyanide groups will be distributed to a certain extent over the π electron system of the phthalocyanine ring due to perpendicular conjugation, thus increasing the electron density over the system. In this respect, long chain alkoxy tin(IV) derivatives would show lines due to their aromatic protons closer to the true positions for most metal phthalocyanines.

CHAPTER 9

THE INFRARED SPECTRA OF SUBSTITUTED PHTHALOCYANINES

A. Introduction

On consideration of the numbers of atoms in the phthalocyanine molecule, the infrared spectra of its derivatives contain relatively few bands and this may be attributed to the high degree of symmetry of the structure. Another useful observation is that variation of the central metal atom in a given series has only a small effect upon the positions of the bands, so a member of a particular series may be quite easily fingerprinted by its spectrum. There are a number of excellent references in the literature tabulating the infrared spectra of phthalocyanines(54)(112)(113), but little work has been done on the correlation of the bands. Elvidge and Lever(54) list vibrations common to a variety of chromium phthalocyanines, and Lever in some unpublished work in this department identified the N-H absorption of phthalocyanine by deuteration. Kroenke and Kenney(79) have studied the spectra of some derivatives of phthalocyanine tin(IV), and have assigned aromatic C-H and benzene ring C-C vibrations. These will be discussed later. Far more work has been done on the porphyrins, and a large number of bands in these compounds have been assigned(114)(115). In this work, the infrared spectra of a number of phthalocyanines, including those described in Chapters 3, 4 and 5, have been studied, and the principal bands are tabulated. Points in common, and differences between series are discussed.

Table VI

Phthalocyanine M	(3-Methyl)$_4$-	(4-Methyl)$_4$-	(4:5-dimethyl)$_4$-
3035 ± 5 (w)	3032 ± 4 (w)	3010 ± 5 (w)	3025 ± 5 (w)
-	2940 ± 4 (w)	2940 ± 5 (w)	2960 ± 5 (w)
-	2902 ± 4 (w)	2902 ± 5 (w)	2898 ± 2 (w)
-	2850 ± 3 (w)	2852 ± 4 (w)	2840 ± 3 (w)
1609 ± 10 (m)	1605 ± 5 (m)	1617 ± 3 (m)	1619 ± 2(w-m)
1500 ± 26 (s)	1511 ± 9(w-m)	1516 ± 10(w-s)	1497 ± 17(m-s)
-	1490 ± 2 (m)	1489 ± 3 (m)	-
1461 ± 12 (m)	1472 ± 5 (m)	-	1466 ± 4(m-s)
-	1438 ± 6 (m)	1451 ± 5 (m)	1436 ± 3 (m)
1420 ± 10(m-s)	1397 ± 5 (m)	1398 ± 5(m-s)	1405 ± 6(m-s)
-	1379 ± 1 (m)	1379 ± 1 (w)	1381 ± 1 (m)
1335 ± 10 (s)	1336 ± 2 (s)	1341 ± 7(m-s)	1344 ± 6(w-s)
-	1323 ± 3 (s)	1322 ± 3(s-m)	1309 ± 6(m-s)
1290 ± 3 (s)	1264 ± 2 (m)	1278 ± 2(m-s)	-
-	1230 ± 4 (m)	-	1245 ± 3 (w)
-	1219 ± 4 (m)	-	-
1203 ± 2 (w)	1205 ± 10 (w)	1202 ± 2 (w)	1219 ± 7 (w)
1165 ± 5(m-s)	1174 ± 2(w-m)	1168 ± 3 (m)	1180 ± 2(w-m)
-	1163 ± 6 (w)	-	-
-	1143 ± 3(w-m)	-	-
1120 ± 4 (s)	1133 ± 5 (m)	1140 ± 2 (m)	1136 ± 3 (w)
-	1122 ± 5 (m)	1132 ± 2 (m)	-
-	1110 ± 6 (w)	-	-
1088 ± 5 (s)	1092 ± 5(m-s)	1093 ± 4 (s)	1101 ± 4 (vs)
1070 ± 8(m-s)	1068 ± 4 (s)	1060 ± 8(m-s)	-
-	1040 ± 5 (w)	1039 ± 3 (w)	1032 ± 9(m-s)
1003 ± 3 (w)	1006 ± 2 (m)	1003 ± 2 (w)	998 ± 2 (w)
905 ± 12(m-s)	941 ± 6 (m)	938 ± 7 (m)	-
-	889 ± 10 (m)	889 ± 7 (m)	882 ± 1(m-s)
-	800 ± 4(m-s)	824 ± 3(m-s)	-
780 ± 4 (m)	-	-	-
774 ± 4 (m)	774 ± 2(m-s)	776 ± 1 (m)	774 ± 2 (w)
-	757 ± 7 (m)	-	755 ± 3(m-s)
760 ± 5(m-s)	744 ± 6 (s)	747 ± 7 (s)	737 ± 5(m-s)
730 ± 5 (s)	733 ± 3 (m)	727 ± 5 (m)	724 ± 4(m-s)
691 ± 2 (w)	681 ± 3 (w)	685 ± 4 (w)	685 ± 1 (w)
672 ± 1 (w)	672 ± 1 (w)	672 ± 1 (w)	672 ± 1 (w)
Metal-free derivative only			
3236 (w)	3246 (w)	3256 (w)	3248 (w)
1535 (w)	1535 (w)	1533 (w)	1540 (w)

B. Tabulation of spectra

In all the compounds studied, the spectroscopic samples were prepared by grinding the phthalocyanine with potassium chloride, and compressing the homogeneous mixture into a disk. All spectra were measured on a Grubb-Parsons D.B.1.Infrared Spectrophotometer.

In Table VI are listed the absorptions (in cm^{-1}) and the frequency limits of the main bands of the metal derivatives of phthalocyanine, tetrakis-3-methyl- , tetrakis-4-methyl- and tetrakis-4:5-dimethylphthalocyanines. As would be expected, substitution of phthalocyanine has led to an increase in the complexity of the spectrum, this being most marked in the case of tetrakis-3-substitution, where much doubling of the bands occurs; and least in the symmetrical tetrakis-4:5-derivatives.

C. Assignments

(i) Aromatic C-H stretching modes. In the tin derivatives which they studied, Kroenke and Kenney assigned a common band at 3030 cm^{-1} to the aromatic C-H stretching mode. This weak band is common to all samples investigated and has an overall range 3005 - 3040cm^{-1}, and there can be no doubt that this assignment is correct.

(ii) C=C in plane stretching modes. Two bands near 1600 and 1500cm^{-1} common to all phthalocyanines studied can safely be assigned to the benzenoid C=C skeletal vibrations. In the

3- and 4-methyl derivatives, there is a third band near 1490cm^{-1}, possibly arising from non-symmetrical substitution. In the 3-methyl derivative, the 1600cm^{-1} band shows slight doubling, and is shifted to lower frequency, this latter observation being in agreement with Colthup's comments on 1:2:3-trisubstituted benzenes(116). A fourth band in the 1460-70cm^{-1} region, overlapping with the CH_3- asymmetrical deformation in the case of the 4-methyl series, can also be assigned as a C=C skeletal vibration. One or more of the bands in this section, however, probably arise from aromatic C=N modes also.

(iii) Aromatic C-H out-of-plane deformations. Unsubstituted phthalocyanines show a very strong band near 730cm^{-1}, which appears as a medium absorption in the methyl derivatives. Kroenke and Kenney assign this band to the aromatic C-H out-of-plane deformation, (which occurs at 776cm^{-1} in phthalonitrile). This band is probably overlapping an additional absorption, which also falls near 730cm^{-1}. 3-Methylphthalonitrile shows a strong band at 801cm^{-1}, due to three adjacent hydrogen atoms, and this appears near 800cm^{-1} in the tetrakis-3-methylphthalocyanines. 4-Methylphthalonitrile has two bands, at 907 and 836cm^{-1} respectively, and as expected, 4:5-dimethylphthalonitrile shows only one, at 900cm^{-1}. These absorptions show up in the corresponding phthalocyanines respectively near 889 and 824cm^{-1} and near 882cm^{-1}.

(iv) Aromatic C-H in-plane deformations. In aromatic compounds, these bands fall in the 1225-950cm^{-1} region, and can give some information regarding the substitution pattern around the aromatic ring. The phthalocyanines show a number of bands in this region of a wide range of intensities, and consequently, no attempt was made to make assignments. However, the pattern of bands in this region varies considerably with substitution, and this will be discussed later.

(v) Aliphatic C-H stretching modes. There are three weak bands in the methyl-substituted phthalocyanines, respectively near 2950, 2900 and 2850cm^{-1}, which may be assigned to the methyl C-H stretching modes. The former, which is also the weakest is assignable to the asymmetrical mode, and the latter two to the symmetrical mode. The symmetrical mode appears as a doublet, with its midpoint near the usual position for this band (2875cm^{-1}), due to the presence of a double bond (aromatic ring) adjacent to the methyl group. Fox and Martin attribute this splitting to a resonance effect(117).

(vi) Aliphatic C-H deformations. A medium intensity band, common to the methyl substituted phthalocyanines, but absent from unsubstituted derivatives, occurring in the 1432-1450cm^{-1} region may be assigned to the asymmetrical C-H deformation of the methyl group. This band is at higher frequency in the 4-methyl series, and overlaps the C=C skeletal vibration which falls in the same region. The band near 1380cm^{-1} is assigned to the symmetrical C-H deformation, as this is the expected position for such a band. There is a band near 1400cm^{-1}, however, common to methyl substituted phthalocyanines. Both of these bands are absent from the spectra of two octakis chloromethyl phthalocyanines studied, and here, the CH_2 deformation falls near 1455cm^{-1}.

(vii) Metal-free phthalocyanines. The spectra of the metal-free phthalocyanines differ in a number of respects from those of the corresponding metallated derivatives, since the central portion of the molecule is no longer held in such a rigid conformation. However, the bands so far discussed should not be affected by such a situation, since they occur as a result of vibrations on the periphery of the molecule. This result is borne out in practice, and the assignments made so far in the earlier sections are paralleled by similar bands of similar intensities in the metal-free parent compounds. This is additional strong evidence in favour of the assignments made.

The N-H stretching mode appears between 3236-56cm^{-1} in agreement with Lever's results. Lever also assigned weak bands at 1534 and 1253cm^{-1} to the N-H deformation modes, the former being observed in the derivatives studied here, but the latter not always being apparent. Mason(114) in some work on porphin assigned the NH stretching mode at 3305cm^{-1} and the deformations at 970 and 719cm^{-1} by deuterating with D_2SO_4 and studying the shifts in the bands. The latter two bands were observed to be strong, but have no obvious counterparts in the metal-free phthalocyanines apart from a strong band which appears between 1004 and 991cm^{-1}. It seems unlikely that Lever would have missed the disappearance of so prominent a band whilst observing shifts in two much weaker ones, so no further conclusions can be drawn without a more detailed study.

(viii) Additional assignments. Comparison of the spectra of tetrakis-4:5-dimethyl- and octakischloromethylphthalocyanine cobalt(II) shows a very large number of bands in common, thus confirming the structure of the latter as tetrakis-4:5-bischloromethylphthalocyanine cobalt(II). The band at 1100cm^{-1}, which is very intense in the case of tetrakis-4:5 disubstitution appears at 1110cm^{-1}, and the 880cm^{-1} band appears near 900cm^{-1}. The C-Cl stretching mode appears as a broad band close to 700cm^{-1}.

(ix) Bands common to all phthalocyanines. In addition to the benzenoid aromatic vibrations already discussed, there are a number of bands common to all the phthalocyanines studied which must arise from skeletal vibrations in the phthalocyanine molecule. These bands are as follows -

1430-1392 (m-s), 1350-1330 (s), 1225-1195 (w)
1105-1083 (s-vs), 1008-996 (w) (strong in metal-free),
777-770 (m), 765-732 (s), 739-720 (m-s) (weak in metal-free),
690-680 (w), 672cm^{-1} (w).

The bands near 1200 and 1000cm^{-1} are probably aromatic C-H in-plane deformations, but the others are more difficult to assign. The band near 1400cm^{-1} may arise from a skeletal vibration of the carbon atoms in the tetrazaporphin ring thought there is little to support such a suggestion. Aromatic tertiary amines show strong C-N absorption between 1360-1310cm^{-1}, which ties in well with the observed strong band near 1340cm^{-1}. It is thus possible that this band arises from the C-N absorption in the isoindole rings, it being shifted to lower frequency, and split into a doublet in the case of the metal-free compounds. Thomas and Martell(115) observe a similar strong band in a series of mesotetraphenylporphyrins, the band having a range 1375-44cm^{-1}, and assigned by them to the =C-N- stretching mode.

(x) The 1180-1020 region. This region provides the best means of assigning methyl substituted metal phthalocyanines to a particular series, since it is very sensitive to the substitution pattern of the molecule. Unsubstituted phthalocyanines show four medium-to-strong sharp bands in this region (1165, 1120, 1088 and 1070cm^{-1}), the centre two being the most intense, this even being true in the case of diphthalocyanine tin(IV). Introduction of methyl groups in the 4-positions has the effect of splitting the second band into two, with corresponding reduction in intensity, and shift to higher frequency; as well as increasing the intensity of the third band, and introducing an additional weak absorption at 1039cm^{-1}.

Addition of four more methyl groups in the 5- positions simplifies the region once more to four bands, but of quite different form from the unsubstituted phthalocyanines.

The sharp bands at 1165 and 1120cm^{-1} appear as aeak absorptions at 1180 and 1136cm^{-1}, the latter showing up once more as a singlet, and the strong 1088cm^{-1} band becomes very intense, whilst moving to 1100cm^{-1}. The weak absorption which appeared at 1039cm^{-1} in the tetrakis-4-methyl series is increased to medium-to-strong intensity, whilst the strong 1070cm^{-1} band disappears altogether, in some cases, but shows as a weak shoulder on the 1100cm^{-1} band in others. This same pattern is apparent in the octakischloromethylphthalocyanines of cobalt(II) and copper(II), only the bands are shifted by 10 - 30cm^{-1} to higher frequency.

The tetrakis-3-methylphthalocyanines present a much more complex picture, there being nine bands in the region. The 1165cm^{-1} band has now become a weak doublet, and the 1120cm^{-1} a roughly symmetrical quartet, centred near 1130cm^{-1}, the outer two lines being weak, and the inner two of medium intensity. The band at 1088cm^{-1} remains as a sharp singlet, as does the one at 1070cm^{-1}, but the intensities are reversed as compared with the unsubstituted phthalocyanines and finally, there is a weak band near 1040cm^{-1}.

It is fruitless to attempt to make assignments in this region without more information being available, but none the less the pattern here presents a useful means of identification of symmetrically substituted phthalocyanines. Perhaps the most interesting band is the one which occurs between 1083-1105cm^{-1} since it varies little in position, and remains prominent, though varying in intensity to some extent with substitution. It would certainly be interesting to know from which vibrational mode it arises.

CHAPTER 10

ULTRAVIOLET AND VISIBLE ABSORPTION SPECTRA

A. Introduction

It was shown in the last chapter that different series of substituted phthalocyanines can be readily distinguished by a study of their infra-red spectra, particularly in the 1180-1040cm^{-1} region. This is not so useful for distinguishing members of a particular series, however, since variation of the central metal atom brings about only small changes in the spectrum. However, in the case of the ultra-violet and visible absorption spectra, the positions of the bands, and their intensities are sensitive to the nature of both the central metal atom, and the substituents around the periphery of the ring. As a result, a study of this region of the spectrum provides the best means of 'finger printing' a particular compound. Listed in this chapter are the visible and near ultra-violet spectra of most of the phthalocyanines prepared in this work, and also for comparison, the ultra-violet spectra of intermediate phthalic anhydrides, -imides and -dinitriles. It is not the purpose of this chapter to assign these bands to particular electronic transitions as this is dealt with elsewhere(118), (119). All measurements here were made with Unicam S.P.500 and S.P.800 spectrophotometers. Except where indicated to the contrary, all wavelengths in this chapter are recorded in Å, and intensities expressed as $\log_{10}\varepsilon$. Points of inflection or shoulders are denoted (i).

B. Phthalic anhydrides

Solutions were prepared by dissolving about 1mg of the anhydride in 10ml of ethanol at room temperature, and completing spectroscopic measurements within half an hour. Measurements were repeated after a further half hour, and showed that negligible opening of the anhydride by the solvent had taken place. The spectra were calibrated using a 'holmium oxide' reference.

Table VII

	1A	1B	1C	2	3A	3B
Phthalic Anhydride	2060(i) 4.430	2125 4.516	2162(i) 4.457	2517 3.615	2887 3.314	2977 3.314
4-Methyl-	2080(i) 4.298	2189 4.492	2227 4.476	2613 3.644	2927 3.356	3018 3.346
4:5-Dimethyl-	2080(i) 4.202	2250(i) 4.527	2275 544	2737 3.659	2920 3.491	3028 3.374
3-Methyl-	2070(i) 4.375	2151 4.528	2187(i) 4.501	2550 3.551	3005 3.456	3094 3.468
3-Isopropyl-4-methyl-	2050(i) 4.179		2242 4.517	2654 3.589	3072 3.511	3148 3.520
3:4:5:6-Tetramethyl-	2050(i) 4.035	2290(i) 4.594	2310 4.612	2786 3.650	3162 3.597	3246 3.648

The spectra of the anhydrides consist of three parts: a triplet (sometimes unresolved), a singlet, and a doublet; and it is interesting to examine the effect of substitution on each of these parts. All the bands of phthalic anhydride experience a bathochromic shift with alkyl substitution, with the exception of band 1A in the last two examples. This shift is larger with 4-substitution, than with 3-substitution; except in the case of the longer wavelength doublet, when the reverse is true; and also, 3-substitution brings about a greater enhancement in band intensity, the exception here being band 2.

C. Phthalimides

Once again, solutions were prepared by dissolving about 1mg of the imide in 10ml of ethanol, measurements being completed as quickly as possible.

Table VIII

	1B	1C	1D	2	3A	3B
Phthalimide	2153 4.591	2342 4.215	2376 4.042		2902 3.253	2969 3.231
4-Methyl-	2229 4.589		2402 4.046			2979 3.275
4:5-Dimethyl-	2260 4.609	2280(i) 4.600	2407(i) 4.010		2925 3.314	
3-Methyl-	2147 4.603	2304 4.114	2387 3.944			3069 3.410
3-Isopropyl-4-methyl-	2234 4.522		2418 3.854	2707 3.232		3109 3.422
N-Chloromethyl-	2196 4.673		2381 3.982		2933 3.240	3004(i) 3.200
N-Ethoxymethyl-	2177 4.633	2287(i) 4.144	2381 3.971		2923 3.258	2984(i) 3.227
Bis-N-Phthalimido-methane	2214 4.849		2383 4.168		2929 3.539	2994(i) 3.503

The imides show a spectrum similar in form to the anhydrides, but in this case band 1A is not resolved, band 2 usually appears as a slight inflection or tailing on 3A, and the longer wavelength doublet is not so well resolved. It is interesting to note that for a given anhydride/imide pair, bands 1B and 3B are in fairly constant positions. 4-substitution in phthalimide brings about a bathochromic shift with little change in intensity, whereas 3-substitution results in a hypsochromic shift at short wavelengths, and a large bathochromic shift at longer wavelengths, the latter being accompanied by an appreciable increase in intensity. N-Substitution on the other hand has little effect on absorption intensities, but brings about appreciable bathochromic shifts in the bands.

D. Phthalonitriles

The ultra-violet spectra of the phthalonitriles are very interesting in that they show a series of low intensity, but very sharp, bands between 2800-3000Å. There is also a triplet about five times as intense between 2350-2550Å, and a very intense band (not recorded here) near 2000Å. The solutions used were of the same concentration, in ethanol, as in the cases of the anhydrides and imides, and the spectra are recorded in table IX. Both methylation and bromomethylation of phthalonitrile has led to a bathochromic shift in all of the bands, and 4-substitution has produced a larger shift than 3-substitution in the shorter wavelength bands, but the converse is true in the series at longer wavelengths. If the bathochromic shifts in the bands due to methyl substitution arise from inductive effects, then one would expect 4-bromomethylphthalonitrile to show a hypsochromic shift. This is not observed in practice, so the shifts are due to some other effect.

Table IX

Phthalonitrile	4-methyl-	4:5-Dimethyl-	3-methyl-	4-Bromomethyl-	4-Pyridiniummethyl Chloride
2330 3.966	2385(i) 4.008	2450(i) 4.026	2350(i) 3.959		2365(i) 4.178
2366 3.970	2432 4.041	2483 4.047	2386 3.991	2470 4.100	2412 4.189
2435 3.842	2483(i) 3.974	2545(i) 3.978	2452 3.906		2462(i) 4.139
					2610 3.757
					2648(i) 3.709
	2735(i) 2.919				
2735(i) 2.974	2760(i) 2.979	2744 2.982	2811(i) 3.193	2780(i) 3.088	
2767 3.009	2787 3.038	2797 3.039	2850(i) 3.281		2795(i) 3.075
2815 3.204	2812 3.218	2842 3.149	2885 3.437	2881 3.243	2850 3.253
2845(i) 3.117	2880 3.132	2891 3.048	2939 3.358		2880(i) 3.191
2908 3.289	2943 3.301	2949 3.152	2986 3.503	2980 3.237	2948 3.323

E. Chloromethylated phthalocyanines

Solutions were prepared by dissolving lmg of the pigment in 100ml of 1-chloronapthalene. The spectra of CuPc and CoPc are included for comparison.

Table X

Phthalocyanines	λ_{max} and Log_{10} ϵ				
CuPc$^{(50)}$	3500 4.76	5880 4.06	6110 4.56	6480 4.51	6780 5.34
$CuPc(CH_2Cl)_{3-4}$ E¦	3520 (583)	5750(i) (70)	6175 (364)	6575(i) (338)	6855 (1921)
$CuPc(CH_2Cl)_6$	3505 4.67		6215 4.46		6915 5.18
$CuPc(CH_2Cl)_7$	3515 4.76	5775(i) 3.81	6220 4.53	6630(i) 4.52	6920 5.25
$CuPc(CH_2Cl)_8$	3515 4.71	5790(i) 3.99	6215 4.55	6585(i) 4.53	6935 5.14
$CuPc(CH_2OH)_3(CH_2Cl)_2$	3445 4.73		6070 4.50	6440 4.46	6770 5.10
CoPc$^{(50)}$	3480 4.65		6065 4.53		6720 5.19
$CoPc(CH_2Cl)_8$	3325 4.77		6180 4.52	6450(i) 4.55	6790 5.09

Introduction of chloromethyl groups has the effect of shifting the bands to longer wavelengths, whilst reducing them in intensity only to a small degree.

F. Pyridinium salts of chloromethylated phthalocyanines

Solutions were prepared by dissolving about 1mg of the salt in 100ml methanol, and the spectra were run as quickly as possible, and in any case, within one hour.

Table XI

Phthalocyanines	λ_{max} and $\mathrm{Log}_{10}\,\epsilon$					
$CuPc(CH_2Cl)_7.2py$			3435 4.65		6340 4.55	6765 4.80
$CuPc(CH_2Cl)_7.3py$	2185 4.78	2580 4.66	3455 4.65	6065(i) 4.42	6375 4.53	6730 4.88
$CuPc(CH_2Cl)_4(CH_2OH)_2.2py$	2170 4.73	2575 4.64	3470 4.57	6130(i) 4.31	6420(i) 4.44	6760 4.69
$CuPc(CH_2OCH_3)_4(CH_2Cl)_4.2py$			3475 4.51	5780(i) 3.93	6500(i) 4.41	6780 4.48
$CuPc(CH_3)_4(CH_2Cl)_4.2py$	2245 4.66	2565 4.62	3490 4.48	6010 4.14	6440(i) 4.34	6785 4.46
$CoPc(CH_2Cl)_7(CH_2OH).2py$	2160 4.68	2550 4.54	3330 4.55	6010(i) 4.18		6650 4.62

The first two ultra violet bands were not recorded in the case of the first and fourth pyridinium salts, but were doubtless present as they are a constant feature in the spectra of these compounds. The structures of the compounds listed are too varied to enable comment to be made on the spectroscopic data, but it is interesting to contrast the di- and tripyridinium salts of heptakischloromethylphthalocyanine copper (II).

G. Tetrakis-4-methylphthalocyanines

Spectra were examined in a number of solvents, and these are indicated. Solutions contained about 1mg of pigment in 100ml of solvent.

Table XII

Derivative	λ_{max} and $\log_{10}\epsilon$							
Cu. (CN)		3560 4.612		5750(i) 3.809		6170 4.564	6580(i) 4.524	6855 5.304
Co (CN)		3500 4.587				6095 4.477		6740 5.091
Co (Py)		3365 4.843				5985 4.482		6620 5.021
Fe (CN) rel.intens.		3350 (1.00)				6000 (0.22)		6640 (1.40)
Fe.2Py (Py) rel.intens.		3340 (1.00)	4110 (0.24)			5980 (0.34)		6585 (0.94)
Fe (MK) rel.intens.	3160 (1.00)	3265 (1.00)	3690 (0.85)	4070 (0.42)		6030 (0.41)	6420(i) (0.53)	6690 (1.50)
Zn.H_2O (DC)		3465 4.828		5720(i) 3.947	5900(i) 4.035	6130 4.504	6535 4.493	6845 5.277
Zn.Py (Py)		3515 4.916				6140 4.641	6525 4.606	6815 5.392
$SnCl_2$ (CN)		3675 4.740		5980(i) 3.512	6150(i) 3.751	6410 4.465	6830(i) 4.402	7130 5.222
$SnCl_2$ (CN) $+C_9H_6O_3$		3690 4.786		5840(i) 3.714	6130(i) 3.894	6340 4.515	6780(i) 4.459	7045 5.257

(CN), 1-chloronapthalene; (DC), o-dichlorobenzene;
(MK), methanolic KCN; (Py), pyridine.

Since the iron compounds were not obtained pure, only the relative intensities of the bands are recorded.

H. Tetrakis-4:5-dimethylphthalocyanines

Without exception, these compounds were too insoluble, even in 1-chloronapthalene to prepare solutions of 1mg sample in 100ml solvent. Consequently, only the relative intensities of the bands are recorded (in parentheses). Also in some cases, in view of the long path lengths required to obtain satisfactory spectra (2-5cm), the solvent caused cut-out before the 3500Å band could be recorded.

Table XIII

Derivative	λ_{max}, (rel.intens.)					
Cu (CN)			5740(i) (0.14)	6170 (0.38)	6570(i) (0.42)	6890 (1.50)
Co (CN)				6100 (0.39)	6505(i) (0.45)	6800 (1.50)
Co (Py)	3405 (1.00)			5985 (0.39)		6640 (1.36)
$SnCl_2$ (CN)	3680 (1.00)	6000(i) (0.06)	6180(i) (0.10)	6425 (0.50)	6890(i) (0.48)	7160 (2.84)

J. Tetrakis-3-methylphthalocyanines

No difficulty was experienced in recording these spectra, the solutions being prepared from 1mg sample and 100ml solvent. Once again, the relative intensities only of the bands of the iron derivatives are recorded, since the compounds were not obtained sufficiently pure.

Table XIV

Derivative	λ_{max} and $\text{Log}_{10}\ \epsilon$						
Cu (CN)	3480 4.956		5750(i) 3.883	5940(i) 4.063	6180 4.572	6595 4.509	6915 5.263
Co (CN)	3530 4.944		5660(i) 3.826		6111 4.468	6520(i) 4.543	6815 5.161
Co (Py)	3280 4.798				6030 4.504		6690 5.033
Fe (CN) Rel.intens.	3380 (1.00)				6080 (0.46)		6710 (1.31)
Fe.2py(Py) Rel.intens.	3330 (1.00)	4140 (0.27)			6010 (0.35)	6370(i) (0.45)	6655 (1.13)
Fe (MK) Rel.intens.	3130 (1.00)	3675 (0.83)	4040(i) (0.47)		6020 (0.37)	6410(i) (0.48)	6680 (1.27)
Zn (CN)	3420 4.824		5740(i) 3.853	5960(i) 3.991	6175 4.515	6600 4.438	6890 5.209
Zn.py (Py)	3550 4.681		5740(i) 3.668	5920(i) 3.872	6165 4.508	6580(i) 4.489	6870 5.267
$SnCl_2$ (CN)	3650 4.653		5970(i) 3.731	6210(i) 3.890	6465 4.528	6940(i) 4.460	7215 5.249

K. The metal-free phthalocyanines

The visible spectra of the methyl substituted metal-free phthalocyanines have been omitted intentionally from the last three sections. They are rather different in some respects from the corresponding metal-substituted derivatives, having two intense bands in the 6500-7000Å region, instead of the usual one band, and are listed together for convenience. The visible spectrum of phthalocyanine itself is also included for comparison(50). Solutions were prepared by dissolving 1mg of the pigment in 100ml 1-chloronapthalene.

Table XV

Derivative	λ_{max} and $\log_{10}\epsilon$							
Phthalocyanine	3500 4.74	5540 3.57		6020 4.43	6360 4.62	6450 4.62	6650 5.18	6980 5.21
(4-Methyl)$_4$-	3445 4.829	5600(i) 3.578	5800(i) 3.924	6030 4.450	6375 4.661	6450 4.664	6645 5.084	7000 5.141
(4:5-Dimethyl)$_4$-		5630(i) 3.636	5820(i) 3.867	6069 4.373	6420 4.564	6485 4.567	6710 5.008	7065 5.077
(3-Methyl)$_4$-	3425 4.768	5650(i) 3.655	5850(i) 3.944	6100 4.446	6430 4.613		6755 5.054	7080 5.092

L. Derivatives of phthalocyanine copper (II)

For completeness, it is worth listing the visible spectra of a number of alkyl substituted phthalocyanines of copper(II), in order to demonstrate the effect of substitution on band positions. Since intensities are not available for all the derivatives, and in one case the position of the 3500Å band is not known, these particular data are omitted.

Table XVI

Derivative	λ_{max}				
CuPc	5670(i)	5880(i)	6110	6480	6780
(4-Me)$_4$CuPc	5750(i)		6170	6580	6855
(4:5-Dime)$_4$CuPc	5740(i)		6170	6570	6890
(3-Me)$_4$CuPc	5750(i)	5940(i)	6180	6595	6915
(4-*iso*bu)$_4$CuPc	5740(i)		6195	6575(i)	6900

M. Discussion

As was stated earlier, it is not the purpose of this chapter to discuss at length the theoretical aspects of the electronic spectra of phthalocyanines. However, some interesting effects of substitution cannot be allowed to pass without comment. These are best listed.

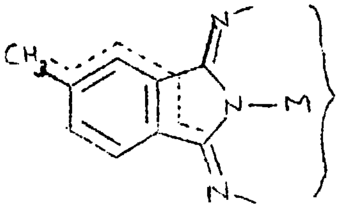
1. A bathochromic shift is observed at the red end of the spectrum when phthalocyanines are substituted both by groups with a positive inductive effect (alkyl functions) and by groups with a negative inductive effect (chloromethyl functions).

2. For a given number of methyl, or chloromethyl groups in the 4- and 5- positions, this shift is of the same order.

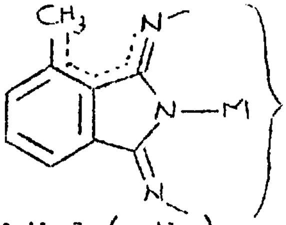
3. Tetrakis-4:5-dimethyl substitution produces a greater shift than tetrakis-4-methyl substitution. This is as expected.

4. Tetrakis-~~4~~3-methyl substitution produces a greater shift even than tetrakis-4:5-dimethyl substitution. This is unexpected.

It may be concluded that these bathochromic shifts are not due to inductive effects, in view of the results obtained from methyl- and chloromethyl- substitution. Such shifts brought about by alkyl substitution are often attributed to hyperconjugation. It is believed in some quarters that hyperconjugation is not feasible in a molecule in the ground state, but can take place in the excited state. Consequently, the energy of the excited state is lowered, and the transition energy for a π-π^* transition shifts to longer wavelengths. Such a concept would explain the bathochromic shifts due to both methyl- and chloromethyl- groups rather well. However, hyperconjugation theory would demand that 4-substitution should bring about a greater shift than 3-substitution, as is borne out in the cases of para- and orthotolunitriles :



4-Methyl (para)



3-Methyl (ortho)

This is precisely the opposite effect to what is observed. Ficken(120) noted that the tetracyclohexenotetrazaporphins showed a greater bathochromic shift than the octamethyltetrazaporphins, when compared with the parent compounds. He states that since a methylene group $-CH_2-R$ shows a weaker hyperconjugative effect than a methyl group $-CH_3$, this result is the reverse of what would be expected, and concludes that hyperconjugation theory breaks down when applied to the tetrazaporphins. Reference to table XVI shows that 4-*iso*butyl substituents result in a greater bathochromic shift than 4-methyl substituents, this effect being basically the same as that observed by Ficken. It thus appears that neither inductive effects, nor hyperconjugation adequately account for the shifts observed in the spectra of substituted phthalocyanines, and some alternative theory must be sought.

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