SOLUBLE PHTHALOCYANINES

AND RELATED COMPOUNDS

A Thesis Submitted to the University of London
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The preparation of a number of soluble derivatives of phthalocyanine has been carried out. These derivatives have been used to study the aromatic ring by proton magnetic resonance spectroscopy. From the results of these studies some conclusions have been made concerning the structure and aromaticity of the phthalocyanine macrocycle.

Specific studies have been carried out on dialkoxy-silicon-phthalocyanines and some evidence has been put forward for the structure of these compounds from proton magnetic resonance studies. Deuteration has been used as a technique to elucidate some ambiguous features of the P.M.R. spectra.

Tetra-alkyl-phthalocyanines have been prepared from alkyl substituted intermediates and have been found to have enhanced solubility in chloroform. Proton magnetic resonance studies indicated that molecular aggregation occurred in concentrated solution.

It has been shown that aggregation is inhibited by substituents in the 5 and 6 co-ordinate positions attached to the central metal and P.M.R. studies on these compounds have proved to be of interest: in particular, di-alkoxy-silicon-tetrakis(4-t-butyl)-phthalocyanines have been examined. Some suggestions have been made as to the effect of substituents upon the aromaticity of the macrocycle.
Peripheral substitution of t-butyl groups has been suggested as a suitable general method for solubilising the macrocycle for P.M.R. studies. In this way, the structure of bis(phthalocyanine)--tin has been investigated and some new evidence for the structure of this compound is presented.

Finally, chemical shifts were used to calculate the aromaticity of the macrocycle, and the results of these calculations are discussed.
ACKNOWLEDGEMENTS

This work was carried out over a period of three years, one spent at Imperial College and two at the University of Surrey. Throughout this period I am very deeply indebted to Professor J.A. Elvidge for his supervision, and for his readiness to offer help and encouragement at all times.

I would like to thank the technical staffs of Imperial College and University of Surrey for their services, and especially Mrs. I. Boston and Mr. J.P. Bloxsidge for Nuclear Magnetic Resonance measurements.

My grateful thanks are also due to Mrs. A. Woods for the neat and efficient typing of this thesis.

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INTRODUCTION

The first record of what must undoubtedly have been phthalocyanine was made in 1907 by Braun and Tcherniac\(^1\). They observed a blue colour when o-cyanobenzamide was fused. In 1927, de Diesbach and von der Weid\(^2\) observed the formation of a blue compound when o-dibromobenzene was heated with cuprous cyanide and pyridine in a sealed tube. They mistakenly identified this as a pyridine complex and were amazed at the thermal stability of the compound. From later evidence it can be concluded that the compound they prepared was copper phthalocyanine.

In 1928, chemists working at Scottish Dyes (Grangemouth) isolated a blue pigment from the vats where phthalimide was prepared from phthalic anhydride and gaseous ammonia. This discovery, and the subsequent formulation of the blue compound by Linstead and his coworkers at Imperial College\(^3, 4, 5, 6, 7\) led to the introduction of one of the most revolutionary chromophores in the dyestuffs industry.

Phthalocyanine is an almost pure spectral blue compound, and as such has proved of great value in the dyestuff and pigment field. The copper derivative of phthalocyanine was marketed in 1934 by I.C.I. as Monastral Blue B S, a very valuable pigment for paints and plastics. The remarkable thermal and light stability of the compound adds to its desirable properties as a pigment. Its insoluo-
bility in paint media is also useful since it gives opacity to the paint film. However the compound had to be made water soluble to be of any use as a textile dyestuff. The aromatic nature of the macrocycle has made sulphonation possible, and conversion to the sodium salt gave a water soluble compound\(^{(8)}\). This technique has been used commercially in the preparation of phthalocyanine acid dyes. Chloromethylation has also been achieved\(^{(9)}\) and subsequent quaternisation with nitrogen and sulphur bases has lead to water soluble derivatives which have substantivity for cellulose. This is the basis of the Alcian dyes of I.C.I. Phthalocyanines have also found use as polymerisation\(^{(10)}\) and oxidation\(^{(11)}\) catalysts, and much work has been done on the photoconducting properties of the compound\(^{(12)}\).

Linstead in the 1930's showed that the blue compound isolated at Scottish Dyes Ltd. was the iron complex of a macrocycle which had a similar basic structural unit to that proposed for the porphyrins\(^{(13)}\). X-ray crystallographic measurements by Robertson, in his classic experiments,\(^{(14, 15, 16)}\) confirmed this structure.

Linstead went on to demonstrate that a large number of metallated phthalocyanines could be prepared by a variety of methods\(^{(17)}\). The phthalocyanine ring has proved a very interesting ligand in co-ordination chemistry due to the rigid planar structure imposed by the four inner ring nitrogen atoms. The more general methods for the preparation of phthalocyanines are illustrated in the following
Reactions III and IV may also be carried out using metal salts or metal oxides. In addition, a further commercial method VI consists in heating a phthalic derivative, normally the anhydride, or alternatively the imide, with urea in the presence of a metal or metal salt and ammonium molybdate or zirconium tetrachloride as catalyst\(^{18,19}\). This is known as the urea melt method for the preparation of phthalocyanines.

The metal free derivative is usually prepared by the demetallation of di-sodium, calcium or magnesium phthalocyanines using acidic conditions. However it can also be prepared from 1,3-diminoisoindoline by heating in a hydrogen donor solvent such
Phthalocyanines owe their commercial importance at least in part to their extremely low solubility in simple solvents. However, this property makes a chemical study of the compound considerably more difficult than it would otherwise be. The aim of this work was to prepare some soluble derivatives of the macrocycle with the object of obtaining P.M.R. spectra. The ultimate goal was a method for the solubilisation of all phthalocyanines, so that the general chemistry of metallated phthalocyanines could be studied by P.M.R. spectroscopy. Also it was thought possible to gain information about the ring current induced by this type of system and provide a measure of the aromaticity of the macrocyclic ring.

The low solubility of phthalocyanine is believed to be due to the very compact nature of the macrocycle. The ring is planar and quite symmetrical. It has been shown by X-ray work\(^{(14)}\), that the phthalocyanine rings tend to stack within the crystal lattice as shown in Fig. I. The interplanar $\text{N-N} \, \text{"bonding"}$ would be absent in the porphyrins and this would explain the considerably higher solubility of porphyrins over phthalocyanines.

It is much easier for the solvent molecules to penetrate the crystal lattice and so force the macrocyclic rings apart.
The approach considered in this work was to attach alkyl chains to the phthalocyanine ring. The effect upon the solubility should be two-fold.

i) To destroy the molecular symmetry of the macrocycle without affecting the aromatic character. The result would be that molecular stacking would become more difficult and the inherent stability of the crystal lattice would be reduced. Hence solvent molecules would be able to penetrate the lattice and allow solvation of the compound.

ii) The hydrophobic nature of the compound would be increased
and hence also its 'oil' solubility.

As a result of these effects, the attachment of alkyl chains to the macrocycle would have little effect upon the solubility in polar solvents but the solubility in non-polar solvents should be increased.

Two methods were available for the introduction of alkyl chains into the phthalocyanine ring.

i) The attachment of alkyl chains to the central metal:- Kenney and his coworkers\(^{(20)}\) have reported the preparation of a number of central metal substituted phthalocyanines, such as the 6-co-ordinate dialkoxy-silicon phthalocyanines, and have shown that these compounds have a much increased solubility in benzene. Also di-alkoxy-germanium compounds have been reported\(^{(21)}\) and di-alkoxy-titanium compounds\(^{(22)}\) but these have not been studied here.

ii) The attachment of alkyl chains to the periphery of the ring:- This method has more advantages than the first since no limitation is placed on the nature of the central metal. However, attempts at direct alkylation of phthalocyanine have lead to mixtures\(^{(23)}\). For our present studies we require compounds of definite constitution. Hence it has been necessary to synthesise substituted phthalocyanines from alkyl substituted precursors of established structure.

Di-alkoxy-silicon-phthalocyanines have been prepared here and have been shown to have high solubility in chloroform. Also tetra
(alkyl)-phthalocyanines have been prepared and these compounds also are extremely soluble in non-polar solvents. A series of compounds have been prepared in which the phthalocyanine ring is substituted both at its periphery and also on the central metal. The solubility of these compounds is extremely high and their P.M.R. spectra have proved most interesting. Lastly, a number of tin-phthalocyanines have been prepared, including bis(phthalocyanine)-tin; and P.M.R. spectroscopy has been used in an attempt to clarify the structure of this unique compound. Some new evidence is presented which indicates that bis(phthalocyanine)-tin has a true "sandwich" structure.
A) Di-Alkox-Silicon-Phthalocyanine Compounds

i) Historical—The silicon phthalocyanine compounds were discovered in 1960 by Kenney and his coworkers\(^{24}\). Earlier attempts, by Linstead, to prepare these compounds in 1936 had failed\(^{17}\). Kenney prepared dichloro-silicon-phthalocyanine by the reaction of 1,3-diminoisoindoline with silicon tetrachloride using quinoline as solvent. The product was isolated as a crystalline solid by filtration of the hot reaction mixture. This compound was hydrolysed to dihydroxy-silicon-phthalocyanine by a number of methods, the most efficient being to reflux dichlorosilicon phthalocyanine with pyridine and 0.88 ammonia. The dihydroxy derivative could then be filtered from the reaction mixture.

It was shown that dihydroxy-silicon-phthalocyanine was a reactive species and would undergo substitution by certain hydroxylic species. Dihydroxy-silicon-phthalocyanine was also found to undergo self condensation with the formation of a polymeric compound. A more interesting reaction however is the formation of di-alkoxy-silicon-phthalocyanines. These are formed by the reaction of dihydroxy-silicon-phthalocyanine with aliphatic alcohols. The factors which influence the reaction are:

i) The acidity of the R-OH reactant.

ii) The strength of the Si-OR link formed.
iii) The insolubility of Pc Si(OH)$_2$ in organic solvents.

iv) The reaction temperature.

It has been stated by Kenny$^\text{(20)}$ that more acidic hydroxylic compounds such as phenol or trichloroethanol will react more readily than less acidic alcohols. It is also possible to displace one residue by another, employing a more acidic alcohol. Thus Pc Si (OCH$_2$C$_6$H$_5$)$_2$ in refluxing benzyl alcohol interacts with triphenylsilanol, to yield the siloxide. The importance of iii) and iv) on the reaction rate is discussed below.

It has been suggested that the most likely mechanism for this reaction involves the formation of siliconium ions$^\text{(20)}$.

\[
\begin{align*}
\text{OH(Pc.Si)OH} & \xrightarrow{R\cdot\text{OH}} \text{OH(Pc.Si)OH} \xrightarrow{\text{H}_2\text{O}} \text{OH(Pc.Si)} \xrightarrow{\text{OR}^-} \text{OH(Pc.Si)OR} \\
\end{align*}
\]

The fact that the acidity of the R-OH reactant is apparently important, and that the siliconium ion can probably delocalise its positive charge into the phthalocyanine ring by use of its $d_{xz}$ and $d_{yz}$ orbitals also fits in with this hypothesis.

It has been shown that the di-alkoxy-silicon-phthalocyanines undergo hydrolysis to a varying degree, depending on the nature of the alkoxy substituent. The hydrolysis rate has been shown to be enhanced by the presence of acid, but little hydrolysis has been
shown to take place in the presence of strong alkali. This suggests that the first stage in the hydrolysis is protonation of the oxygen atom. Subsequently, there is scission of the weakened bridge.

An interesting feature of two di-alkoxy-silicon-phthalocyanines reported is the low melting points of these compounds. Phthalocyanine compounds in general, are extremely thermally stable, and this rather peculiar feature is undoubtedly a result of bulky groups reducing the inherent stability of the phthalocyanine crystal lattice. The solubility of these compounds in non-polar solvents is also increased and this feature is believed to be due to the instability of the crystal lattice. The bulky groups tend to push the aromatic rings apart and allow solvent molecules to penetrate the crystal lattice.

The somewhat increased solubility of di-alkoxy-silicon-phthalocyanines makes them potentially interesting compounds for use in P.M.R. studies. Methods have been found whereby the solubility of di-alkoxy-silicon-phthalocyanines can be increased greatly, and these methods are described below.

ii) Discussion:-- Certain di-alkoxy-silicon-phthalocyanine compounds have been reported where increases in solubility have been noticed. These include di-alkoxy-silicon-phthalocyanines where the alkyl group is a simple straight carbon chain. These compounds
would be of interest if their P.M.R. spectra could be obtained. However, all the compounds reported have a solubility which is too low to be of any use in this respect. It was thought that the field held sufficient possibilities for further work.

Bis(octadecan-1-oxy)-silicon-phthalocyanine has been reported by Kenney (20) as a crystalline compound m.p. 152°, and having increased solubility in benzene. This compound has been prepared and has been used as a basis for the preparation of much more soluble derivatives.

1,3-Diiminoisandozoline was prepared by the reaction of 2-phthalonitrile with liquid ammonia in an autoclave (26). It was converted to dichloro-silicon-phthalocyanine by heating with silicon tetrachloride, in quinoline (27).

N.B. The above diagramatic representation for phthalocyanine will be used throughout this thesis. Investigations of dichloro-silicon-phthalocyanine have shown that the chlorine atoms are also reactive, and so hydrolysis to
dihydroxy-silicon-phthalocyanine is unnecessary. Dichloro-silicon-
phthalocyanine was allowed to react with a number of alcohols in
refluxing xylene for three days, and in all cases, where this
method was used, the yield of di-alkoxy-silicon-phthalocyanine
was high. The long reaction times, which are needed for high
yields, are apparently due to the very low solubility of dichloro-
silicon-phthalocyanine in the reaction medium. The solvent
used was sodium dried, so that hydrogen chloride gas would be
expelled from the solution during the reaction.

In all cases the work up procedure was the same. The xylene
solvent was removed by distillation under reduced pressure and the
product was dissolved in benzene. The benzene solution was
chromatographed on alumina (Brockmann activity: 2) using a benzene
eluent. The highly polar impurities tended to be adsorbed, and
the much less polar phthalocyanine passed down the column. The
eluent was collected and evaporated to dryness. The product was
crystallised from light petroleum. The di-alkoxy-silicon-
phthalocyanine crystallised as blue-green needles with a red reflex.

Bis(octadecan-1-oxy)-silicon-phthalocyanine was prepared by a
similar procedure to the above. Although its solubility was
considerably higher than most known phthalocyanines, it was too
insoluble for P.M.R. work. Bis(octan-1-oxy)-silicon-phthalocyanine
has been prepared by Kenney(20) and bis(octan-2-oxy)-silicon-
phthalocyanine has been prepared here, but both compounds have a
solubility which is considerably lower than bis(octadecan-1-oxy)-silicon-phthalocyanine.

However bis(decan-1-oxy)-silicon-phthalocyanine has been prepared and the solubility of this compound is considerably higher than either the eight or eighteen carbon chain derivatives. It appears that, so far as saturated alkyl chains are concerned, there is an optimum chain length above which the solubility decreases. It appears that at this point, the steric effect is less important and molecular weight considerations begin to apply. The effect is summarised in Fig. II.

![Fig. II](image)

The steric effect of the alkyl chain can be increased by reducing the degrees of freedom of the alkyl chain. Hence by introducing a double bond into the alkyl chain, it becomes more rigid and more difficult to stack within the crystal lattice. An important
feature is that this occurs without any increase in molecular weight. Hence it may be expected that unsaturated alcohols should react with dichloro-silicon-phthalocyanine to give di-alkoxy compounds having greatly increased solubility.

This has been found to be so; and furthermore it has been shown that the effect is more pronounced in the case of cis olefins than trans. The relative solubility of a number of di-alkoxy-silicon-phthalocyanines is shown in Table I. Bis(octadecan-1-oxy)-silicon-phthalocyanine being the only known compound of the series, is taken as having unit solubility.

**TABLE I**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Relative Solubility (Petrol 60-80); 22°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bis(octadecan-1-oxy)-silicon-phthalocyanine</td>
<td>1</td>
</tr>
<tr>
<td>Bis(octadecan-9(cis)en-1-oxy)-silicon-phthalocyanine</td>
<td>270</td>
</tr>
<tr>
<td>Bis(octadecan-9(trans)en-1-oxy)-silicon-phthalocyanine</td>
<td>6.3</td>
</tr>
<tr>
<td>Bis(decan-1-oxy)-silicon-phthalocyanine</td>
<td>1.6</td>
</tr>
<tr>
<td>Bis(hex-10-en-1-oxy)-silicon-phthalocyanine</td>
<td>13.8</td>
</tr>
</tbody>
</table>

The low melting point of long chain di-alkoxy-silicon-phthalocyanine has been attributed to the steric effect of the alkyl chain within the crystal lattice. However it appears, from the compounds prepared, that the criteria affecting solubility are not the
same with respect to melting point. i.e. Though the solubility of bis(octadecan-1-oxy)-silicon-phthalocyanine is less than bis(decan-1-oxy)-silicon-phthalocyanine, its melting point is considerably lower. It must be stressed that though an optimum chain length has not been observed for low melting point phthalocyanines, it may well occur at even longer chain lengths, and there is room for further work here.

The effect of unsaturation within the chains is as expected. The melting points decrease in the order: saturated \( \geq \) trans-unsaturated \( \geq \) cis-unsaturated. The results are summarised in Table II.

**TABLE II**

<table>
<thead>
<tr>
<th></th>
<th>Melting Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bis(octadecan-1-oxy)-</td>
<td>155</td>
</tr>
<tr>
<td>silicon-phthalocyanine</td>
<td></td>
</tr>
<tr>
<td>Bis(octadec-9( trans)en-1-oxy)</td>
<td>134-135</td>
</tr>
<tr>
<td>silicon-phthalocyanine</td>
<td></td>
</tr>
<tr>
<td>Bis(octadec-9(cis)en-1-oxy)-</td>
<td>125</td>
</tr>
<tr>
<td>silicon-phthalocyanine</td>
<td></td>
</tr>
<tr>
<td>Bis(decan-1-oxy)-</td>
<td>207</td>
</tr>
<tr>
<td>silicon-phthalocyanine</td>
<td></td>
</tr>
<tr>
<td>Bis(undec-10-en-1-oxy)-</td>
<td>174</td>
</tr>
<tr>
<td>silicon-phthalocyanine</td>
<td></td>
</tr>
</tbody>
</table>

It has been shown that many long chain di-alkoxy-silicon-phthalocyanines tend to decompose slowly above 200°. The decom-
position products are suspected to be the long chain alcohol and a polymeric silicon phthalocyanine.

A number of experiments have been carried out in the preparation of long chain di-alkoxy-silicon-phthalocyanines where the alkoxy group contains a substituent other than a double bond. One compound has been prepared in which the alkoxy group contains a terminal ethyl ester grouping. It has been shown that the effect upon solubility and melting point is similar to the presence of a double bond, but even more pronounced. The results summarised in Table III give the solubilities relative to bis(octadecan-1-oxy)-silicon-phthalocyanine.

### TABLE III

<table>
<thead>
<tr>
<th>Compound</th>
<th>Rel. Sol. (petrol 60-80°C)</th>
<th>Melting point °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bis(11-carbethoxy-undecan-1-oxy)Si Pc</td>
<td>42</td>
<td>145</td>
</tr>
<tr>
<td>Bis(undec-10-en-1-oxy)Si Pc</td>
<td>13.8</td>
<td>174</td>
</tr>
</tbody>
</table>

iii) **Interlocking Ring Compounds**—The preparation of a number of long chain di-alkoxy-silicon-phthalocyanines have been described.
It is apparent from molecular models that the fifth methylene group will overlap the edge of the phthalocyanine ring, with the chain in a fully extended conformation. The compounds are effectively a very long 'alkyl' chain with a phthalocyanine unit centrally substituted and perpendicular to the direction of the chain at that point. It is useful to consider the relative sizes of the constituent groupings in these compounds. For example, the phthalocyanine unit in bis(octadecan-1-oxy)-silicon-phthalocyanine is a relatively small part of the bulk of the molecule.

Because of the length of the alkyl chain compared with the size of the phthalocyanine ring, there is the possibility of linking the alkyl chains outside the aromatic ring, so producing an interlocking ring phthalocyanine.
This compound would be of interest for a P.M.R. study because the protons associated with the alkyl chain, would, at different points along the chain suffer both shielding and dishielding. From the ratio of shielded to deshielded protons it should be possible to assess fairly precisely the diamagnetic anisotropy of the phthalocyanine ring.

The acyloin reaction was used in an attempt to ring close bis(11-carbethoxy-undecan-1-oxy)-silicon-phthalocyanine. The reaction is notable for its use in the formation of large rings\(^{(28)}\). Only a few milligrams of a green product were isolated however, and this was shown by T.L.C. to be a mixture of several compounds. It appeared that, under the reaction conditions used, the Si-O bonds had undergone scission.

However, this remains a potentially very interesting possibility and other methods of ring closure might be more successful in attaining it.

**B) Proton Magnetic Resonance Studies**

i) **Historical:** Phthalocyanine is an aromatic macrocycle, and as such is interesting for proton magnetic resonance study. The effect of the induced magnetic field associated with the \(\pi\)-electron system on the proton magnetic resonance spectra of aromatic compounds is well known. Similar effects would be expected for phthalocyanine.
Becker (29) in 1960 prepared a solution of phthalocyanine in deuteriosulphuric acid, and obtained a proton magnetic resonance spectrum in this solvent. He observed a broad doublet at 0.41 and 1.48. However, the pigment almost certainly existed in solution as the di-cation and as a result the observed bands would be to lower field than the true position for phthalocyanine. The central N-H protons would not appear in this spectrum because of proton exchange with the solvent.

Later work by Lever (30), and by Sammes (31) has made use of the dicyanoferre complex of FeII phthalocyanine to study P.M.R. spectra.

Iron II Phthalocyanine complexes with KCN in methanol to give a Dipotassium dicyanoferre complex which is soluble in methanolic KCN. The P.M.R. spectrum was obtained in this solvent, and the broad doublet observed by Becker (29) appeared resolved into an AA'XX' second order splitting pattern. The spectrum was analysed by Sammes and the coupling constants of the system reported (32). The observed chemical shifts of 0.87 and 2.18 for the aromatic protons were to higher field than those reported by Becker, since phthalocyanine in this complex is not protonated. Even so it is doubtful if these bands reported are the true chemical shifts for the aromatic
protons of phthalocyanine. The cyanide groups are co-ordinated to the iron atom, so forming an octahedral complex. The negative charge of the dicyano-ferrate anion will probably be delocalised over the \( \pi \) -electron system of the phthalocyanine ring. Hence the observed chemical shifts will probably be to higher field than the true phthalocyanine aromatic bands.

The best way to overcome this delocalisation of charge would be to prepare soluble derivatives of phthalocyanine which are non-ionic in character. These would need to be soluble in chloroform and carbon tetrachloride, the best solvents for P.M.R. work. The only reports of any compounds satisfying these requirements appeared in the literature during the course of this work. Kenney and his coworkers (33, 34) have reported the preparation of silicon and germanium phthalocyanine compounds which had been solubilised by a series of bulky organosiloxy groups. They have reported the P.M.R. spectra of a number of those complex compounds in solvents such as \( \text{CCl}_4 \) and \( \text{CDCl}_3 \). Of particular interest is Methyl-chlorosilicon phthalocyanine which had been solubilised by causing it to react with a complex organosilanol.

The compound prepared is illustrated below:-

\[
\begin{align*}
\text{CH}_3 \\
\text{Si} \\
\text{O}_3\text{SiCF}_3 \\
(\text{OSi(CH}_3)_3)_2
\end{align*}
\]
The protons on the methyl group appear to come to resonance at 16.33T. This high field shift is undoubtedly due to the high degree of shielding associated with their position immediately above the aromatic ring. Similar effects have been observed in the porphyrin series\(^{(35)}\). This in turn confirms the aromatic nature of the macrocycle.

The aromatic protons associated with the phthalocyanine ring have been quoted as coming to resonance at 0.29T and 1.66T. These values are intermediate between the values reported by Becker and those of Sammes. They are more likely to be the true chemical shifts of the aromatic protons of phthalocyanine.

The spectra of these silicon phthalocyanines has not been fully analysed however, although the chemical shifts are given. The work given in this section makes use of long chain alkoxy groups as solubilising groups, and it must be emphasised that no work on the P.M.R. spectra of silicon phthalocyanines had been reported when this work was carried out.

ii) Proton Magnetic Resonance Spectra of di-alkoxy-silicon-phthalocyanines:– It has been shown that the solubility of di-alkoxy-silicon-phthalocyanines can be greatly increased by a number of methods without resorting to specific solubilising groups. Bis(decan-1-oxy)-silicon phthalocyanine was prepared by the reaction of decyl alcohol with dichloro-silicon-phthalocyanine. The compound
was found to have considerably higher solubility in non-polar solvents than any di-alkoxy-silicon-phthalocyanines reported in the literature. The solubility of this compound was sufficiently high in chloroform and carbon tetrachloride, to give P.M.R. spectra. The spectra reported in this section were all run on the 'Varian A60', 60 Mc/s spectrometer, and in many cases were run at elevated temperature to increase the solubility.

The spectrum of bis(dodecan-1-oxy)-silicon-phthalocyanine is conveniently considered in two parts:

i) The low field aromatic region.

ii) The higher field aliphatic region.

i) Aromatic Region:

At first sight the spectrum appeared to be subdivided into two symmetrical quarters centred at 0.43\(\tau\) and 1.78\(\tau\). Closer examination however revealed that there were at least six lines in each group and the spectrum was treated as an \(AA'XX'\) second order case.

The theoretical \(AA'XX'\) second order spectrum consists of twelve lines corresponding to interactions between \(A\) and \(A'\), \(A\) and \(X\), \(A\) and \(X'\), \(X\) and \(X'\). By making suitable measurements and approximations from
the spectrum, it was possible to calculate the coupling constants for the system. This data is tabulated in Table IV.

TABLE IV

<table>
<thead>
<tr>
<th>Chemical Shift</th>
<th>Coupling Constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_x = 493.5 \text{ c/s (1.78T)}$</td>
<td>$J_{AX} = J_{A \times} \times = 7.81 \text{ c/s}$</td>
</tr>
<tr>
<td>$\nu_A = 574.0 \text{ c/s (0.43T)}$</td>
<td>$J_{XX} = 7.05 \text{ c/s}$</td>
</tr>
<tr>
<td>$\delta_{AX} = 80.5 \text{ c/s (1.35 ppm)}$</td>
<td>$J_{A \times} = J_{AX} \times = 1.09 \text{ c/s}$</td>
</tr>
<tr>
<td>$J_{A1} = 0.55 \text{ c/s}$</td>
<td></td>
</tr>
</tbody>
</table>

The theoretical spectrum was calculated and found to fit very closely with the original. The spectra are shown in Fig. III.

As expected the chemical shifts of the aromatic protons lies between the values observed by Becker and by Sammes, indicating that these chemical shifts are nearer the true value for phthalocyanine. The values obtained are quite similar to those obtained by Kenney\(^{33}\) although the chemical shifts reported here appear to slightly higher field. The difference between the $A$ and $X$ values is a measure of the deshielding effect and hence the aromaticity of the system. The figure obtained of 1.35 p.p.m. is very close to the values obtained by Sammes in the Dipotassium dicyanoferrate system.
Fig III

OBSERVED SPECTRUM

CALCULATED $AA^1XX^1$ SPECTRUM
Aliphatic Region:

The decanoxy chains associated with the phthalocyanine ring and covalently bound to silicon appear as a broad band upfield of 8.5T. An interesting feature is that this broad band extends to higher field than 10T. There are in fact three broad but distinct bands centred at 10.5T, 11.5T and 12T (Fig. IVa). The integration of these broad peaks indicated that they corresponded to four, eight and four protons respectively. It has been deduced that the three bands originated from the protons of the first four methylene groups along each chain, nearest to the silicon atom.

When an aromatic compound is placed within a magnetic field, induced precessional motions of the electrons set up a diamagnetic field (i.e. one which opposes the applied field at the centre of the ring.
Fig. IV

T.M.S. OBSERVED SPECTRUM (a)

T.M.S. OBSERVED SPECTRUM (b)

T.M.S. OBSERVED SPECTRUM (c)
system). Outside the periphery of the ring the secondary induced field is parallel to that applied, as shown in the above diagram. Hence protons held on the periphery of the ring will experience the additive effects of both applied and induced fields. The apparent resonance position is, as a result, lower than the expected position of a proton in a similar non-aromatic environment. The opposite effect is observed when a proton is held above the centre of an aromatic ring. The actual field experienced by the proton is less than the applied field because of the subtractive effect of the induced field. Hence protons held in such an environment will appear to resonate at higher field.

The first four methylene groups along the alkoxy chain are believed to exist in such an environment, and so would be expected to resonate at high field. It has been shown by molecular models that the first four methylene groups along the alkyl chain cannot possibly overlap the edge of the phthalocyanine ring even with the chain in its fully extended conformation. In this position, the fifth group appears to overlap the bridge nitrogen atoms. Only with further methylene groups is the periphery of the ring exceeded. So only these last methylenes will give normal, or possibly low field, signals.

For molecules in solution, the alkyl chain will constantly be moving and will suffer different shielding every instant. Hence an 'average' chemical shift is observed. Since methylene groups
numbers five onwards will, for a period of time, suffer some
deshielding, the expected average chemical shift for these will be
considerably lower than for the groups numbers one to four.

![Graph showing chemical shift vs. methylene groups along the chain.]

However it would appear that the measured chemical shift is not
a true average. The broadening of the lines is not a function of
the resolution since the low field aromatic region appears highly
resolved. It is concluded that in solution the alkyl chains move
relatively slowly and the individual resonance positions tend to be
observed corresponding to a particular conformation. The distri-
bution, and the maximum indicates the chemical shift of the most
likely conformer.

A precise assignment of the high field peaks to the individual
methylene groups was somewhat difficult. The first methylene group
along the chain would be expected to suffer the greatest shielding
since it is nearest to the centre of the aromatic ring. However this
group is adjacent to a more electronegative oxygen atom and a down-
field shift would be expected. The magnitude and extent of these
opposite effects was not known, and so actual assignments could hardly be made without a further study.

Attempts were made to prepare compounds having a sulphur bridge instead of oxygen in the hope that the decrease in electronegativity would cause an upfield shift of the first methylene group and so make assignments possible. However, though the required compound appeared to be formed during the reaction it unexpectedly decomposed upon work up. Specific deuteration was then examined as a means to detailed interpretation of the P.M.R. spectrum.

iii) Deuterated Di-Alkoxo-Silicon-Phthalocyanines:

Deuteration of organic compounds has frequently been carried out to simplify proton magnetic resonance spectra. The deuteron, although magnetic, comes to resonance at a different frequency from the proton, at a given field strength, and hence does not give signals in a P.M.R. spectrum. Also the splitting pattern associated with proton-proton spin-spin interactions are simplified since there is only weak or effectively no coupling to deuterium.

The simplest method of deuterating the methylene groups along the alkyl chain in these compounds was to substitute deuterium into the chain of the chosen alcohol prior to reaction with dichloro-silicon-phthalocyanine. The long chain alcohol selected was undec-10-en-1-ol for two reasons:
i) The high solubility of bis(undec-10-en-1-oxy)-silicon-phthalocyanine.

ii) Undec-10-en-1-oic acid was readily available in a pure state.

α-Deuteration:

Undec-10-en-1,1-d_2-1-ol was prepared by the reduction of the ethyl ester of undec-10-en-1-oic acid using lithium aluminium deuteride. The product was made to react with dichloro-silicon-phthalocyanine to give bis(undec-10-en-1,1-d_2-1-oxy)-silicon-phthalocyanine. The P.M.R. spectrum of this compound (Fig. IVb) clearly lacked the high field peak at 12.09£ which was present in the spectrum of the undeuterated species. It could thus be concluded that this high field peak was due to the α-methylene group, in spite of its position adjacent to oxygen.

The second broad band corresponding to eight protons was seen to show some fine structure in the spectrum of the α-dideuteric compound. An approximation to a triplet at 11.6£ could be seen and was tentatively assigned to the β-methylene group, the splitting resulting from coupling to the two protons of the adjacent γ-methylene group.

In order to confirm these suppositions a further specific deuteration, this time of the β-methylene group, was attempted.
Undec-10-en-1-oic acid was converted into its acid chloride by use of thionyl chloride, and the secondary amido prepared by reaction with N-methyl-aniline\(^{(36)}\).

\[
\text{CH}_2=\text{CH}-(\text{CH}_2)_8\text{CO}_2\text{H} \rightarrow \text{CH}_2=\text{CH}-(\text{CH}_2)_8\text{COC}1 \rightarrow \text{CH}_2=\text{CH}-(\text{CH}_2)_8\text{CONCH}_3
\]

The N-methyl anilide was reduced using lithium aluminium hydride at \(0^\circ\text{C}\)\(^{(36)}\) to give undec-10-en-1-al. The aldehyde was deuterated on the \(\beta\)-carbon atom by a base catalysed enol-exchange reaction in D\(_2\)O/dioxan solution\(^{(37)}\).

\[
\text{CH}_2=\text{CH}-(\text{CH}_2)_8\text{CONCH}_3 \rightarrow \text{CH}_2=\text{CH}-(\text{CH}_2)_8\text{CHO} \rightarrow \text{CH}_2=\text{CH}-(\text{CH}_2)_7\text{CD}_2\text{CHO} \leftarrow \frac{2 \text{ steps}}{\text{D}_2\text{O}} \text{CH}_2=\text{CH}-(\text{CH}_2)_7\text{CH}=\text{CH}-\text{O}^{-} + \text{HOD}
\]

Deuteration was shown to have taken place by P.M.R. spectroscopy.

\[
\begin{align*}
\text{CH}_2 & \quad \text{CH} \\ \\
\text{CH} & \quad \text{CH} \\ \\
(\text{CH}_2)_7 & \quad (\text{CH}_2)_7 \\ \\
\text{CH}_2 & \rightarrow \text{Multiplet} \\ \\
\text{CHO} & \rightarrow \text{Triplet}
\end{align*}
\quad
\begin{align*}
\text{CH}_2 & \quad \text{CH} \\ \\
(\text{CH}_2)_7 & \quad (\text{CH}_2)_7 \\ \\
\text{CD}_2 & \rightarrow \text{Disappeared} \\ \\
\text{CHO} & \rightarrow \text{Singlet}
\end{align*}
\]
Undec-10-en-2,2-d₂-1-al was reduced to the corresponding alcohol using lithium aluminium hydride, and the alcohol was allowed to react with dichloro-silicon-phthalocyanine to give bis(undec-10-en-2,2-d₂-1-oxy)-silicon-phthalocyanine.

The P.M.R. spectrum of the compound is shown in Fig. IVc. The high field peak which was believed to be due to the α-methylene group appeared as an approximate singlet at 12.09 τ. This confirmed the original supposition, since there would be no coupling to the β-deuterated methylene group. The γ-methylene group appeared as a very rough triplet at 11.46 τ due to coupling with the next methylene along the chain. The integration of the spectrum also confirmed this interpretation. It was concluded that the broad band at 10.48 τ, which remained unaltered in the deuterated product, was due to the δ-methylene group.

It is noteworthy that the peaks are somewhat broadened. This is believed to be due to the relatively slow movement of the chain, and not to poor resolution.

By substituting the protons on the α and β-methylene groups with deuterium it has thus been possible to assign unambiguously the high field peaks in the P.M.R. spectra of di-alkoxy-silicon-phthalocyanines. The results are summarised in Table V.

From theoretical considerations discussed so far it might be expected that the shielding associated with the phthalocyanine ring
would fall off rapidly with distance from the centre of the ring. Hence it seemed likely that a regular downfield chemical shift would be observed for the methylenes along the alkyl chain.

**TABLE V**

<table>
<thead>
<tr>
<th>Chemical Shift (( \tau ))</th>
<th>12.09</th>
<th>11.61</th>
<th>11.46</th>
<th>10.48</th>
</tr>
</thead>
<tbody>
<tr>
<td>c/s to higher field than T.M.S.</td>
<td>125.4</td>
<td>96.6</td>
<td>67.5</td>
<td>28.6</td>
</tr>
</tbody>
</table>

From the observed results this would appear to be essentially correct. However, there were appreciable anomalies. Firstly, the abnormally high resonance position of the first four methylene groups has already been explained earlier. Secondly, a downfield shift is observed between \( \alpha \) - and \( \beta \) -methylene groups and between \( \gamma \) and \( \delta \) methylene groups as expected, but the chemical shifts of the \( \beta \) and \( \gamma \) groups are remarkably similar.

This phenomenon can be explained in terms of the preferred conformation of the alkyl chain (Fig. V).
The direction of bonds 'a' and 'b' are rigidly fixed by the bond angle of the oxygen atom. Free rotation about bond 'a' is immaterial. Free rotation about bond 'b' is hardly possible because the long alkyl chain would approach too close to the aromatic ring. The most likely conformation of bond 'b' is as shown in Fig. V. Since the oxygen bond angle is 104.5° and the carbon bond angle 109.5°, bond 'c' will be almost vertical and nearly parallel to the Si-O bond. Hence the α- and β-methylene protons will be at distinctly different average distances above the plane of the aromatic system. This explains the great difference in chemical shift between the α- and β-methylene groups. On the other hand, the β- and γ-methylene protons will on average both occupy the
same region of space, there being free rotation about bonds 'c', 'd' and 'e', and so the similarity in their chemical shifts can be explained. Further along the chain, the steric limitations upon the movement of the chain become less and the expected regular decrease in chemical shift with position should occur. This is observed.

iv) Chain substituted di-alkoxy-silicon-phthalocyanines:

It has been shown earlier that substitution of groups within the alkyl chains of di-alkoxy-silicon-phthalocyanines tends to increase the solubility and depress the melting point of these compounds. Their high solubility makes them especially suitable for P.M.R. study, and use has been made of this when deuterated phthalocyanines were prepared. No mention has been made so far concerning the resonance position of the olefinic protons associated with the undecenoxy chains. It has been found that in all the olefinic compounds used, the protons associated with the double bond do not suffer any shielding. It appears that the shielding region of the aromatic ring does not, to any noticeable extent, extend a distance of ten carbon atoms along the chain.

This feature has also been noticed in the terminal carbethoxy compounds which has been prepared. The protons of the ethyl ester do not appear to suffer any shielding.
The substitution of groups within the chains also leads to low melting compounds. A P.M.R. spectrum was obtained of bis(octadec-9(cis)en-1-oxy)-silicon-phthalocyanine in the liquid phase at 130°. Unfortunately however the liquid was extremely viscous, as would be expected, and so the resolution was low.

C) Experimental

All analyses given in this section were carried out in the Organic Chemistry Department Microanalytical Laboratory of Imperial College, unless otherwise stated.

1,3-Diiminoisoindoline

Phthalonitrile (20g) was stirred with methanol (120ml) and liquid ammonia (40ml) was cautiously added. The mixture was transferred to an enamel lined autoclave (1 l capacity) and heated at 100° for four hours. After cooling, the autoclave was opened and the solution was filtered to remove phthalocyanine impurity.
The filtrate was concentrated by distillation under reduced pressure and upon cooling yielded 1,3-diminoisoindoline as a pale green crystalline solid, m.p. 187°, Lit 194-5°(26). Yield 18 g (79%).

**Dichloro-silicon-phthalocyanine** (27)

1,3-Diminoisoindoline (9.1 g) was heated with silicon tetra-chloride (10.4 ml) and quinoline (104 ml) in a Wood's metal bath. The flask was equipped with a reflux condenser and a mechanical stirrer and the mixture was heated slowly to 220° during 30 minutes. It was maintained at 220° for a further 30 minutes. The solution was seen to turn green and gradually darkened, depositing a purple crystalline solid. The mixture was cooled to 180-190° and was filtered hot (Whatman No. 541). Dichloro-silicon-phthalocyanine was collected as a green crystalline solid with a red reflex. It was washed well with quinoline, benzene, methanol and finally acetone. Yield 7.0 g (73%).

**Bis(octadecan-1-oxy)-silicon-phthalocyanine**

Dichloro-silicon-phthalocyanine (500 mg) was mixed with octadecan-1-ol (4.0 g) and the mixture was heated at 150° in a slow stream of nitrogen for 3 hours. The mass was then heated with acetone (ca 25 ml) for several minutes and filtered. The solid was washed well with acetone. The solid was then extracted with benzene (100 ml) and the benzene solution concentrated to 30 ml. The solution was introduced on to an alumina chromatography column and
eluted with benzene. The fast moving blue-green band was collected. Bis(octadecan-1-oxy)-silicon-phthalocyanine crystallised when the solution was concentrated. The compound was crystallised from petroleum (b.p. 60-80°), m.p. 154°; Lit 152°(20). Yield 127 mg, (14.5%).

\[
\begin{align*}
\text{C}_{68}\text{H}_{90}\text{N}_8\text{Si}_2 & \text{ requires } C = 75.68 \quad H = 8.41 \quad N = 10.39 \% \\
\text{Found} & \quad C = 75.06 \quad H = 8.13 \quad N = 10.53 \%
\end{align*}
\]

Bis(decan-1-oxy)-silicon-phthalocyanine

Dichloro-silicon-phthalocyanine (1.0 g) was added to boiling decan-1-ol (25 ml) and the mixture refluxed for 1½ hours. The product was allowed to cool and was diluted with benzene (25 ml). The benzene solution was filtered and the solid was extracted with benzene. The mixed benzene solutions were chromatographed on alumina, using benzene as eluent. The fast moving blue-green band was collected and concentrated by distillation. Bis(decan-1-oxy)-silicon-phthalocyanine crystallised from the solution. The product was recrystallised from petroleum (b.p. 60-80°) as blue needles with a red reflex, m.p. 207°. Yield 260 mg (19.5%).

\[
\begin{align*}
\text{C}_{52}\text{H}_{58}\text{N}_8\text{Si}_2 & \text{ requires } C = 73.03 \quad H = 6.83 \quad N = 13.11 \quad Si = 3.28 \% \\
\text{Found} & \quad C = 73.42 \quad H = 6.96 \quad N = 12.65 \quad Si = 3.95 \%
\end{align*}
\]

(This analysis was carried out by Dr. A. Bernhardt, Mulheim (Ruhr), Germany.)
Bis(octadec-9(cis)-en-1-oxy)-silicon-phthalocyanine

Dichloro-silicon-phthalocyanine (500 mg) was heated with oleyl alcohol (5 ml) at 200° for 1½ hours. A slow stream of nitrogen was passed through the mixture during the period of heating. The mixture was allowed to cool overnight. It was filtered, and the solid washed well with acetone. The solid was extracted with benzene (50 ml) and the solution chromatographed on alumina using benzene as eluent. The fast moving blue-green band was collected and evaporated to dryness. The solid was crystallised from petroleum (b.p. 60-80°) as needles m.p. 125°. Yield 270 mg (31%).

C₆₈ H₈₆ N₈ Si O₂ requires C = 76.02 H = 8.08 N = 10.40 %
Found  C = 75.97 H = 7.74 N = 10.65 %

Bis (octadec-9(trans)-en-1-oxy)-silicon-phthalocyanine

a) Ethyl octadec-9(trans)-enoate

Elaidic acid (10.5 g) was dissolved in a mixture of absolute ethanol (14 ml) and toluene (8.5 ml) and concentrated hydrochloric acid (0.2 ml) was added. The solution was distilled from a steam bath until the temperature of the azeotrope reached 80°. A further portion of ethanol (14 ml) and toluene (8.5 ml) was added and the distillate again collected. A third amount of ethanol (8.5 ml) and toluene (5.7 ml) was added and the procedure repeated. The residual solvent was then removed under reduced pressure and the
product was vacuum distilled, b.p. 147-150°/0.2 mm; Lit 208-210°/13 mm (38). Yield 9.2 g (80.0%).

b) Octadec-9(trans)-en-1-ol

Lithium aluminium hydride (1.1 g) was slurried with dry ether (25 ml) and ethyl octadec-9(trans)-enoate (9.2 g) in ether (25 ml) was added dropwise with stirring. The solution was then stirred for a further 30 minutes and the excess L.A.H. destroyed by methyl-acetate. The sticky mass was worked up with water and concentrated sulphuric acid (2.5 ml). The ether layer was separated, dried and distilled. Octadec-9(trans)-en-1-ol distilled b.p. 154-158°/0.5 mm. Lit 216/18 mm (39). Yield 7.2 g (89%).

c) Bis(octadec-9(trans)-en-1-oxy)-silicon-phthalocyanine

Dichloro-silicon-phthalocyanine (500 mg) was heated with octadec-9(trans)-en-1-ol (1 g) in dry xylene (25 ml) at reflux for 3 days. The product was evaporated to dryness, and dissolved in benzene (20 ml). The solution was filtered and chromatographed on alumina using benzene as eluent. The fast moving blue-green band was collected and the solution evaporated to dryness. The residue was crystallised from petroleum (b.p. 60-80°) giving bis(octadec-9 (trans)-en-1-oxy)-silicon-phthalocyanine as blue needles with a red reflex, m.p. 134-135°. Yield 720 mg (80%).

C_{68}H_{86}N_{8}Si_{2}O_{2} requires C = 75.94 H = 8.06 N = 10.42 Si = 2.61%

Found C = 75.62 H = 8.08 N = 9.71 Si = 2.71%
(This analysis was carried out by Dr. A Bernhardt, Mulheim (Ruhr), Germany.)

Bis(undec-10-en-1-oxy)-silicon-phthalocyanine

a) Ethyl Undec-10-enate

Undec-10-en-1-oic acid (133 g) was dissolved in a mixture of toluene (166 ml) and absolute ethanol (276 ml) and concentrated hydrochloric acid (3.3 ml) was added. The mixture was distilled and the distillate collected until the temperature of the azeotrope reached 80°C. A further amount of ethanol (276 ml) and toluene (166 ml) was added and the procedure repeated. A third amount of ethanol (166 ml) and toluene (113 ml) was added and the mixture distilled. The residual solvent was removed by distillation under reduced pressure and the residue vacuum distilled giving ethyl undec-10-enenate, b.p. 130-132°/12 mm, n_D^25 1.4379 Lit b.p. 131.5°/16 mm, n_D^23 1.4449(40). Yield 141 g (92%).

b) Undec-10-en-1-ol

Lithium aluminium hydride (5.5 g) was slurried in small portions with dry ether (125 ml) in a flask flushed with nitrogen. Ethyl undec-10-enenate (54.3 g) in dry ether (125 ml) was added dropwise, with stirring, so that the ether refluxed gently. After the addition, the excess L.A.H. was destroyed with methyl acetate. The sticky mass was poured on to a mixture of ice (125 g) and concen-
trated sulphuric acid (12.5 ml). The ethereal layer was separated and the aqueous layer was extracted with ether (2 x 200 ml). The mixed ether extracts were dried over magnesium sulphate and distilled. Undec-10-en-1-ol was collected b.p. 130-132°/15 mm; $n_D^{24.5} 1.4465; \text{Lit b.p. } 132-3/15 \text{ mm}; n_D^{19} 1.4506(40)$. Yield 36 g (83%).

c) Bis(undec-10-en-1-oxy)-silicon-phthalocyanine

Dichloro-silicon-phthalocyanine (500 mg) was added to undec-10-en-1-ol (41 ml) and nitrogen was bubbled slowly through the mixture. The mixture was heated for 3 hours at 150° and it began to crystallise. It was filtered, washed with acetone and the solid was extracted with benzene (100 ml). The benzene extract was chromatographed on alumina using a benzene eluent. The fast moving blue-green band was collected, yielding bis(undec-10-en-1-oxy)-silicon-phthalocyanine, m.p. 175°, upon crystallisation from the eluate. Yield 225 mg (32%).

$C_{54}H_{58}N_8SiO_2$ requires $C = 73.77$ $H = 6.65$ $N = 12.76$ $Si = 3.19\%$

Found $C = 74.32$ $H = 6.64$ $N = 12.90$ $Si = 3.53\%$

Bis(11-carbethoxy-undecan-1-oxy)-silicon-phthalocyanine

a) 11-Bromo-undecan-1-oic acid

Undec-10-en-1-oic acid (redistilled b.p. 122°/0.66 mm) (42.0 g) was dissolved in benzene (500 ml). The solution was cooled in ice
to 5° and a gentle stream of hydrogen bromide gas was bubbled through the solution so that the temperature remained at 5°. The pink solution was concentrated under reduced pressure to about 80 ml, and was allowed to crystallise. The mother liquors were collected and crystallisation repeated. The product was recrystallised from petroleum (b.p. 60-80°), m.p. 50°; Lit 51°(41). Yield 42.5 g (70%).

b) 11-Hydroxy-undecan-1-oic acid

11-Bromo-undecan-1-oic acid (20 g) was added to 10% sodium hydroxide solution (400 ml) and the mixture refluxed gently for 30 minutes. The solution was poured on to cold water (600 ml) and acidified carefully with concentrated hydrochloric acid. The precipitated solid was filtered, washed with water, dried, and recrystallised from benzene. 11-Hydroxy-undecan-1-oic acid was deposited as needles m.p. 65-66°; Lit m.p. 68-69°(42). Yield 13 g (87%).

c) Ethyl (11-hydroxy)-undecanoate

11-Hydroxy-undecan-1-oic acid (5 g) was heated on a water bath with absolute ethanol (25 ml), toluene (15 ml) and a few drops of concentrated hydrochloric acid. The distillate was collected at 75°. Three further amounts of a mixture of toluene (15 ml) and absolute ethanol (25 ml) were added and the procedure repeated each time. The solvent was removed by distillation under reduced pressure and the product was vacuum distilled. Ethyl (11-hydroxy)-undecanoate
was collected b.p. 136-138°/0.5 mm; \( n_D^{26} \) 1.4463; Lit. b.p. 111-112.5°/0.1 mm; \( n_D^{20} \) 1.4478. Yield 4.5 g (79%).

d) Bis (11-carbethoxy-undecan-1-oxy)-silicon-phthalocyanine

Ethyl (11-hydroxy)-undecanoate (4.5 ml) was dissolved in dry xylen (20 ml) and dichloro-silicon-phthalocyanine (500 mg) was added. The mixture was refluxed in a stream of dry nitrogen for 3 days. The xylen was removed by distillation under reduced pressure and the solid was extracted with dry benzene (50 ml). The benzene solution was chromatographed on alumina using 2% methanol in benzene as eluent. The fast moving blue-green band was collected. It was evaporated to dryness and the product was crystallised from petroleum (b.p. 60-80°). Bis(11-carbethoxy undecan-1-oxy)-silicon-phthalocyanine crystallised as blue needles with a red reflex m.p. 144°. Yield 377 mg (46%).

\( \text{C}_{58} \text{H}_{66} \text{N}_8 \text{Si}_6 \) requires C = 69.71 H = 6.66 N = 11.21 %

Found C = 69.63 H = 6.75 N = 11.12 %

2-Hydroxy-cyclodecanone

The apparatus was baked prior to use, and assembled with the use of drying tubes. Dry Xylene (50 ml) and crust free sodium metal were introduced into the apparatus and the apparatus purged with dry nitrogen overnight. The xylen was heated to reflux and the sodium was highly dispersed by rapid stirring (ca 3,000 r.p.m.).
Diethyl sebacate (5 g) in dry xylene was added dropwise over 24 hours. The solution was stirred for a further hour and then cooled in an ice bath. A solution of acetic acid (4.5 ml) in dry ether (10 ml) was added dropwise over 30 minutes and the temperature was allowed to rise to 20°. The precipitated sodium acetate was filtered and washed well with xylene. The xylene solution and washings were combined and the solvent removed by distillation under reduced pressure. The residue was vacuum distilled giving 2-hydroxycyclo-decanone b.p. 129-133°/10 mm; \( n_D^{23.9} 1.4874 \); Lit. b.p. 124-127°/10 mm, \( n_D^{55} 1.4803(44) \). The liquid solidified after long standing. Yield 1.0 g (30.4%).

**Attempted Cyclisation of Bis(11-carbethoxy-undecan-1-ox)-silicon phthalocyanine**

The apparatus and chemicals were dried and purified as described above. Sodium (0.9 g) was dispersed in boiling xylene (25 ml), and bis(11-carbethoxy-undecan-1-ox)-silicon-phthalocyanine (200 mg) in xylene (60 ml) was added dropwise over 30 hours. The reaction mixture became coloured very deep purple. Stirring was continued for a further hour at reflux after the addition was complete. The reaction mixture was cooled in an ice bath and acetic acid (2.5 ml) in ether (10 ml) was added slowly with stirring. The deep purple colour immediately turned dark green on addition of acetic acid. The mixture was stirred for several minutes and was then filtered. The solid was washed with xylene and the filtrate
and washings were combined. The green solution was evaporated to dryness under reduced pressure, leaving a green tar. Methanol (ca 5 mls) was added and a green solid was precipitated. The solid was shown to consist of at least five compounds, by T.L.C. The product could not be further identified since only 3 mgms had been obtained.

**Bis(docanthio)-silicon-phthalocyanine**

a) 1-Bromo-decane

Decan-1-ol (33 g) and purified red phosphorus (1.6 g) were placed in a 3-necked flask. Bromine (19 g) was added dropwise and the reaction mixture was heated at 100° for 10 minutes. The mixture was allowed to cool and water (50 ml) was added; and then ether (70 ml). The phosphorus was filtered from the solution and the ethereal layer was separated. The aqueous layer was extracted with ether (2 x 50 ml) and the ether extracts dried over anhydrous potassium carbonate. The ether was removed by distillation from a water bath and the residue was vacuum distilled. 1-Bromo-decane was collected b.p. 112-114°/15 mm; Lit 117.6-118°/15.5 mm (45). Yield 30.5 g (66%).

b) Decan-1-thiol

1-Bromo-decane (21 g) was mixed with a solution of thiourea (9.5 g) in water (6.2 ml) and the mixture was refluxed gently for
2 hours. The solution became homogeneous after about 30 minutes. A solution of sodium hydroxide (7.5 g) in water (75 ml) was added and the solution was stirred under reflux for a further 2 hours. The thiol was seen to separate above the aqueous phase. Decan-1-thiol was separated from the aqueous layer and the latter was extracted with ether (2 x 20 ml). The mixed thiol and other extracts were dried over anhydrous sodium sulphate. The ether was removed by distillation and the residue was vacuum distilled. Decan-1-thiol was collected at 106-108°/13 mm; Lit 96-97°5 mm\(^{(46)}\). Yield 12.2 g (74.4%).

c) Bis(deman-1-thio)-silicon-phthalocyanine

Decan-1-thiol (5 ml) was heated with dichloro-silicon-phthalocyanine (500 mg) at 200° for 5 hours. A slow stream of nitrogen was passed through the mixture. The solution appeared to gradually turn blue-green in colour and HCl gas appeared to be evolved. The product was dissolved in benzene, filtered and chromatographed on alumina using benzene as eluent. Only about 2-3 mgms. of product could be isolated and this appeared to decompose rapidly to an insoluble blue material. The product was not further identified.

Undec-10-en-1,1-d\(_2\)-1-ol

Lithium aluminium deuteride (400 mg) was dissolved in dry ether
(10 ml) and ethyl undec-10-enate (3.0 g) in dry ether (10 ml) was added dropwise. The mixture was stirred and the ester was added at such a rate that the solvent refluxed gently. When addition was complete, methyl acetate (1 ml) was added to destroy any L.A.D. remaining. The sticky mass was transferred to a beaker containing crushed ice (10 g) and concentrated sulphuric acid (1 ml). The solution was stirred and the ether layer separated. The aqueous layer was extracted with ether (3 x 20 ml) and the mixed extracts were dried over magnesium sulphate. The ether was removed by distillation and undec-10-en-1,1-d_{2}-1-ol was vacuum distilled, b.p. 107°C/3.8 mm; n_{D}^{25} 1.4464. Yield 1.85 g (76%).

Bis(undec-10-en-1,1-d_{2}-1-oxy)-silicon-phthalocyanine

Undec-10-en-1,1-d_{2}-1-ol (1g) was dissolved in dry xylene (25 ml) and dichloro-silicon-phthalocyanine (500 mg) was added. The mixture was refluxed, with stirring, for 3 days. The mixture was then filtered and the filtrate evaporated to dryness under reduced pressure. The residue was dissolved in benzene and chromatographed on alumina using benzene as eluent. The benzene was removed by rotary evaporation and the product was crystallised from petroleum (b.p. 60-80°C); m.p. 174-175°C. Yield 470 mg (65%).

Undec-10-en-2,2-d_{2}-1-ol

a) Undec-10-en-1-oyl chloride

Undec-10-en-1-oic acid (50 g) and thionyl chloride (71 g)
were refluxed gently until evolution of hydrogen chloride had ceased, (2\frac{1}{2} hours). The excess thionyl chloride was removed by distillation under reduced pressure and the residue was vacuum distilled. Undec-10-en-1-oyl chloride was collected, b.p. 88°/0.6 mm; n_D^{24} 1.4545; lit b.p. 74-78°/0.1 mm; n_D^{23} 1.4530\textsuperscript{(36)}. Yield 47.0 g (85.3%).

b) Undec-10-en-1-(N-methyl) anilide

Undec-10-en-1-oyl chloride (34 g) was dissolved in benzene (50 ml) and a solution of N-methyl-aniline (22 g) in pyridine (22 ml) was added slowly, with shaking. The mixture was allowed to stand for 30 minutes, and water (75 ml) was added. The layers were separated and the aqueous layer was extracted with benzene (2 x 35 ml). The combined benzene extracts were washed with 2-N Hydrochloric acid (100 ml), and then with distilled water. The benzene layer was dried over anhydrous sodium sulphate and distilled. The anilide was collected as a yellow oil, b.p. 157-161°/0.5 mm; n_D^{24} 1.5073; lit. n_D^{22} 1.5070\textsuperscript{(36)}. Yield 40.8 g (88.5%).

c) Undec-10-en-1-al (36)

Lithium aluminium hydride (1.7 g) in dry ether (100 ml) was added slowly to a solution of the above anilide (38.5 g) in dry ether (100 ml). The mixture was kept stirred in an ice bath for 3 hours. The excess L.A.H. was decomposed by the addition of ethyl acetate (20 ml). The complex was decomposed by the addition
of 10% hydrochloric acid (100 ml) and the ethereal layer was
separated. The aqueous layer was extracted with ether (2 x 50 ml)
and the combined ether extracts were washed with 2-N hydrochloric
acid (100 ml) and then with water (100 ml). The ethereal layer was
dried over anhydrous sodium sulphate and the ether removed by
distillation. The residue was vacuum distilled and the aldehyde
collected b.p. 66-70°/0.5 mm \( n_D^{24.5} \) 1.4430. Some anilide (7.4 g)
was recovered b.p. 152-157°/0.5 mm. Yield (on unrecovered anilide),
11 g (58%).

d) Undec-10-en-2,2-d₁₉-1-al (37)

Undec-10-en-1-al (10 g) was dissolved in dioxan (25 ml) and
deuterium oxide (Norsk Hydro, 99.8% D₂O) (5 ml) was added.
Anhydrous potassium carbonate (60 mg) was also added and the mixture
was refluxed for 50 hours. N.B. Drying tubes were fitted to the
apparatus to avoid exchange with atmospheric moisture. The
mixture was immiscible at room temperature but became miscible at
reflux. The 'water'/dioxan mixture was removed by distillation and
the residue was vacuum distilled to regenerate the partially
deuterated aldehyde.

The distillate (b.p. 66-70°/0.5 mm) was refluxed for a further
50 hours under the same conditions as the above, to complete the
exchange. The 'water'/dioxan mixture was removed by slow dist-
illation and the aldehyde vacuum distilled again; b.p. 63-64°(0.4 mm)
\( n_D^{22} \) 1.4436. Yield 4.0 g (40%).
Lithium aluminium hydride (287 mg) was warmed with dry ether (10 ml) and undec-10-en-2,2-d$_2$-1-ol (3.7 g) in dry ether (10 ml) was added dropwise over a period of 10 minutes. The mixture was then stirred for a further 10 minutes and the excess L.A.H. was decomposed with methyl acetate (0.5 g). The sticky mass was added to crushed ice (20 g) and concentrated sulphuric acid (1 ml) and the ethereal layer was separated. The aqueous layer was extracted with ether (2 x 10 ml) and the ether extracts dried over magnesium sulphate. The ether was removed by distillation and the residue vacuum distilled. The deuterated alcohol was collected b.p. 79-80°/0.5 mm; $n_D^{24}$ 1.4493. Yield 3.1 g (83%).

**Bis(undec-10-en-2,2-d$_2$-1-oxy)-silicon-phthalocyanine**

Undec-10-en-2,2-d$_2$-1-ol (1 ml) was dissolved in dry xylene (25 ml) and dichloro-silicon-phthalocyanine (500 mg) was added. The mixture was refluxed for 3 days with a slow stream of nitrogen bubbling through the apparatus. The mixture was filtered and the unreacted dichloro-silicon-phthalocyanine was weighed (270 mg). The solvent was removed by distillation under reduced pressure and the solid was dissolved in benzene. The solution was chromatographed on alumina and the eluate was evaporated to dryness. The product was recrystallised from petroleum (b.p. 60-80°) as blue needles m.p. 177°. Yield 206 mg (77% on unrecovered dichloro-silicon-phthalocyanine).
SECTION II
A) Introduction

Phthalocyanines, which have considerably increased solubility in non-polar solvents have been prepared commercially, and have been widely used in printing inks. The solubilisation of these compounds has been achieved by the attachment of alkyl chains around the periphery of the ring. This has normally been carried out by chloromethylation of phthalocyanine followed by reaction with an aralkyl compound in the presence of aluminium chloride\(^{(47)}\).

The reason for this increased solubility may be threefold.

i) Bulky groups attached to the macrocycle prevent the aromatic rings from stacking in the crystal and so reduce its inherent stability.

ii) The presence of solvent "attracting" groups in the molecule.

iii) The presence of a large number of positional isomers resulting from the original chloromethylation.

The presence of a large number of positional isomers is an obvious disadvantage in this approach. It has been shown that separation of the isomers of chloromethylated phthalocyanine is very difficult\(^{(48)}\) and hence this method of alkylating phthalocyanine was rejected.
A more suitable method of preparation of peripherally substituted phthalocyanines would be to make use of alkyl substituted precursors. Some work on this subject has been carried out by Sammes and this approach appeared to hold some promise. By using methyl substituted phthalonitrile, Sammes produced pigments having noticeably increased solubility in aromatic solvents. Also, from P.M.R. spectra of dipotassium tetrakis (methyl)-phthalocyanine dicyanoferate, some evidence was also obtained that the substituted pigment was a single isomer. The alkyl side chain appeared to have some directing influence on the way the o-phthalic units linked up.

It has been shown that symmetrical substituents around the phthalocyanine ring do not lead to more soluble compounds. This is presumably due to the retention of symmetry in the molecule, and consequent stabilisation of the crystal lattice. Work by Sammes also showed that substitution in the 4-position appeared to have more effect upon the solubility than substituents in the 3-position.

It was decided to extend the work carried out by Sammes using somewhat larger substituent groups. It appeared from the above reasoning that satisfactorily soluble phthalocyanines should be obtained by synthesis from o-phthalic units bearing a single substituent in the 4-position. Furthermore it had been shown by Sammes that substituents in the 3-position tended to cause
difficulties in synthesis if the group was larger than methyl, apparently due to steric effects; i.e. The opening of a five membered ring, which is an essential part of the proposed \( \text{o-dinitrile} \) synthesis, is extremely difficult if the \( 3 \)-substituent is large\(^{(52)} \). This difficulty in opening sterically hindered five membered rings has been observed before\(^{(53)} \).

\[
\begin{align*}
R &\quad O \\
\bigg\{egin{array}{c}
\text{HN} \\
\text{NH}
\end{array}igg\} &\xrightarrow{\text{If } R\text{CH}_3} & R \\
\bigg\{egin{array}{c}
\text{CONH}_2 \\
\text{CONH}_2
\end{array}igg\}
\end{align*}
\]

It was believed from general principles that, as in the \( \text{di-alkoxy-silicon-phthalocyanines} \), there would be an optimum chain length, above which the solubility of the pigment would decrease. It was not clear what this optimum chain length was likely to be, since only two alkyl chains were involved in the silicon derivatives and four chains would be involved here. Since two chains of ten carbon atoms were found to give optimum conditions for solubility in the silicon phthalocyanines, it was thought that four chains of five carbon atoms may be a reasonable analogy for peripheral substitution.

Chain branching was expected to increase the solubility of the alkyl substituted phthalocyanines because of the increased bulkiness of the group. However it has been shown that there appears to be little difference whether the chain is straight or branched. Both \( n \)-pentyl and \( t \)-butyl substituted phthalocyanines have been prepared.
and both have been shown to have very high solubility in non-polar solvents. Any differences in solubility are only slight and no conclusions can be drawn.

B) Tetras(4-n-pentyl)-phthalocyanines

It was proposed that 4-n-pentyl phthalonitrile would serve as a precursor to alkyl substituted phthalocyanines which would have considerably increased solubility in non-polar solvents. 4-Alkyl phthalic derivatives have been little studied to date where the alkyl group is larger than ethyl. The synthesis which was devised was based upon the Diels-Alder reaction of a 2-alkyl substituted diene with maleic anhydride to give a reduced 4-alkyl phthalic anhydride.

\[
\begin{array}{c}
\text{R} \\
\text{C=C} \\
\text{C=C} \\
\end{array} + \begin{array}{c}
\text{O} \\
\text{C=O} \\
\text{C=O} \\
\end{array} \rightarrow \begin{array}{c}
\text{R} \\
\text{C=C} \\
\text{C=O} \\
\end{array}
\]

The reaction appeared to be fairly general for alkyl substituents although the synthesis involved a large number of steps.

Synthesis of 4-n-pentyl phthalonitrile

The starting material which was 1-heptanal was readily available. It was subjected to a Mannich reaction using formaldehyde and dimethylamino hydrochloride\(^{54}\). The Mannich intermediate was not isolated but steam distillation of the reaction mixture caused it
to undergo Hofmann elimination to give 2-n-pentyl acrolein.

\[
\begin{align*}
\text{CH}_3(\text{CH}_2)_4 \text{CH}_2 \text{CHO} & \rightarrow \text{CH}_3(\text{CH}_2)_4 \text{CH} \text{CHO} \rightarrow \text{CH}_3(\text{CH}_2)_4 \text{C} \text{CHO} \\
& \text{CH}_2 \quad \text{CH}_2
\end{align*}
\]

\[N(\text{CH}_3)_2 \text{HCl}\]

The 2-n-pentyl acrolein was collected by vacuum fractionation.

The product was allowed to react with methyl magnesium iodide in anhydrous ether, under standard Grignard reaction conditions. The complex was decomposed by hydrochloric acid and the product, 2-n-pentyl-3-hydroxy-1-butene was distilled

\[
\begin{align*}
\text{CH}_3(\text{CH}_2)_4 \text{C} \text{CHO} & \rightarrow \text{CH}_3(\text{CH}_2)_4 \text{C} \text{CH} \text{OH} \\
& \text{CH}_2 \quad \text{CH}_2 \quad \text{CH}_3
\end{align*}
\]

Attempts were made to dehydrate the secondary alcohol in a catalytic vapour phase reaction over alumina\(^{(55)}\). The secondary alcohol was passed down a heated silica tube packed with alumina chips. The pyrosylate was then washed and distilled to give a diene fraction.

\[
\begin{align*}
\text{CH}_3(\text{CH}_2)_4 \text{C} \cdots \text{CHOH} & \rightarrow \text{CH}_3(\text{CH}_2)_4 \text{C} \cdots \text{CH} \\
& \text{CH}_2 \quad \text{CH}_3 \quad \text{CH}_2 \quad \text{CH}_2
\end{align*}
\]

From the P.M.R. spectrum of this fraction it was suspected that a mixture of dienes were present. Base catalysed proton transfer would cause isomerisation of the above 2-alkyl butadiene to a more
stable octadiene derivative

\[
\begin{align*}
\text{I} & : \quad \begin{array}{c}
\text{CH}_3(\text{CH}_2)_3 - \text{CH}_2 - \text{C} - \text{CH} \\
\end{array} \\
\text{II} & : \quad \begin{array}{c}
\text{CH}_3(\text{CH}_2)_3 - \text{CH} = \text{C} - \text{CH} \\
\end{array}
\end{align*}
\]

The signal due to the methyl group on the double bond in structure II appeared as a singlet at 8.07 in the P.M.R. spectrum. Also the ratio of olefinic to non-olefinic protons was too low to support structure I and too high to support structure II.

If a similar base catalysed proton transfer were to occur with the starting material then one would expect some 3-methyl-octan-2-one to be formed

\[
\begin{align*}
\text{I} & : \quad \begin{array}{c}
\text{CH}_3(\text{CH}_2)_4 - \text{C} - \text{CH} \text{OH} \\
\end{array} \\
\text{II} & : \quad \begin{array}{c}
\text{CH}_3(\text{CH}_2)_4 - \text{C} = \text{C} - \text{OH} \\
\end{array}
\end{align*}
\]

It was found, by distillation of a further fraction, after collection of the diene, that 3-methyl-octan-2-one was obtained in quite high yield. This compound was characterised by preparation of its 2,4-dinitrophenylhydrazone and its semicarbazone. Also the P.M.R. spectrum of the compound was exactly as expected.
for this structure.

\[
\begin{align*}
\text{CH}_3 & \rightarrow \text{Triplet} \quad 9.1 \tau \quad (3p) \\
(CH_2)_4 & \rightarrow \text{Broad Band} \quad 8.75 \tau \quad (8p) \\
\text{CH} & \rightarrow \text{Multiplet} \quad 7.52 \tau \quad (1p) \\
\text{CH}_3 & \rightarrow \text{Doublet} \quad 8.98 \tau \quad (3p) \\
\text{C} = \text{O} & \\
\text{CH}_3 & \rightarrow \text{Singlet} \quad 7.96 \tau \quad (3p)
\end{align*}
\]

Similar rearrangements to the above have been noticed in related compounds \((56, 57)\).

Since 2-n-penty1-buta-1,3-diene was required quite pure, this method was unsatisfactory. It was decided to pyrolyse the acetate as this reaction was known to be less likely to cause isomerisation. 2-n-penty1-3-hydroxy-1-butene was acetylated using acetic anhydride and pyridine. The acetate was then pyrolysed over glass balls by distilling it into a pyrolysis tube in a stream of nitrogen.

\[
\begin{align*}
\text{CH}_3 (\text{CH}_2)_4 & -C-\text{CH} \text{OH} \rightarrow \text{CH}_3 (\text{CH}_2)_4 & -C-\text{CHO}_2 \text{C} \text{CH}_3 \rightarrow \text{CH}_3 (\text{CH}_2)_4 & -C-\text{CH} \\
\text{CH}_2 & \text{CH}_3 \quad \| & \text{CH}_2 & \text{CH}_3 \quad \| & \text{CH}_2 & \text{CH}_2
\end{align*}
\]

The apparatus is shown in Fig. VI
The pyrolysate was collected and was washed with sodium hydroxide solution. It was then fractionated and the recovered acetate was recycled. The process was repeated five times and the 2-n-pentyl-buta-1,3-diene was refractionated.

The P.M.R. spectrum of the diene indicated an approximate ABX system for the olefinic region, with a broadened singlet superimposed. The broadened singlet was assigned to the in-chain terminal methylene group of the diene and the ABX system to the vinyl grouping. The ABX system was analysed and the results are shown in Table VI.

2-n-pentyl-buta-1,3-diene was allowed to react with maleic anhydride to form the Diels-Alder adduct 4-n-pentyl-1,2,3,6-tetra-
hydrophthalic anhydride.

\[
\text{\includegraphics{hydrophthalic_anhydride.png}}
\]

**TABLE VI**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
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<tbody>
<tr>
<td><strong>V&lt;sub&gt;A&lt;/sub&gt;</strong> = 309.3 c/s</td>
<td><strong>J&lt;sub&gt;AX&lt;/sub&gt;</strong> = 17.7 c/s</td>
</tr>
<tr>
<td><strong>V&lt;sub&gt;B&lt;/sub&gt;</strong> = 297.7 c/s</td>
<td><strong>J&lt;sub&gt;BX&lt;/sub&gt;</strong> = 11.1 c/s</td>
</tr>
<tr>
<td><strong>V&lt;sub&gt;X&lt;/sub&gt;</strong> = 380.0 c/s</td>
<td><strong>J&lt;sub&gt;AB&lt;/sub&gt;</strong> = 1.4 c/s</td>
</tr>
</tbody>
</table>

* from T.M.S. at 60 Mc/sec.

Attempts were made to aromatise this compound catalytically using 30% palladium on charcoal as dehydrogenation catalyst(58). The system which was used is illustrated in Fig. VII.

The reduced anhydride was heated in refluxing naphthalene and a stream of dry carbon dioxide was passed through the apparatus to sweep away any hydrogen. The gases were collected over 30% Potassium hydroxide solution which would react with the CO<sub>2</sub> and allow any hydrogen to be collected. However, only a very small amount of 4-n-pentyl-
Phththalic anhydride could be obtained from the reaction. It was characterised by its infra-red spectrum which was identical with an authentic sample prepared later. The amount of catalyst required was very large compared with the amount of material that was used. Hence it appeared to be a very uneconomical method of obtaining 4-n-pentyl phthalic anhydride, and was abandoned.

An apparently better method of aromatisation was by oxidative bromination. 4-n-pentyl-1,2,3,6-tetrahydrophthalic anhydride was brominated using elemental bromine in acetic acid. Dehydrobromination was effected by removing the solvent and heating the residue at 200° for several hours. Hydrogen bromide was evolved, and distillation of the black tar which remained yielded 4-n-pentyl-phthalic anhydride.
4-n-pentyl-phthalic anhydride was converted into 4-n-pentyl phthalimide by initially reacting it with 0.88 ammonia solution. The water and excess ammonia were then boiled off and the residue heated slowly to 250°. Upon cooling, the imide crystallised.

4-n-pentyl phthalimide was prepared from the imide by stirring with 0.88 ammonia solution for 24 hours, and was dehydrated by passing phosgene gas through a pyridine solution of the di-amide. 4-n-pentyl-phthalonitrile was collected by distillation, as a colourless oil.

Tetrakis(4-n-pentyl)-phthalocyanines

Tetrakis(4-n-pentyl)-phthalocyanine was prepared by the demetallation of tetrakis(4-n-pentyl)-phthalocyanine-disodium. The disodium derivative was prepared from sodium amyloxide and 4-n-pentyl-phthalonitrile using standard conditions. The disodium derivative which was formed was demetallated by refluxing with 50% acetic acid. The metal free pigment was shown to be extremely soluble in non-polar solvents and was purified by chromatography on
alumina (Broekmann activity 2), using benzene as eluent.

The product could not be obtained crystalline although it was found to be analytically pure as it was collected from the chromatography column. The reason for this may be due to the presence of a number of positional isomers. However all attempts to prove the presence of isomers by chromatography failed.

Work has been carried out on tetrakis(alkyl)-tetrazaporphins by Lewis (64), using substituents which included methyl and neo-pentyl groups. He observed that no separation was possible of the isomers of tetrakis-methyl-tetrazaporphin. However he was able to effect a partial separation of the positional isomers of tetrakis-neo-pentyl-tetrazaporphin using T.L.C. or column chromatography. Since the method of preparation of tetrazaporphin is similar to that of phthalocyanine it can be reasonably suggested that the tetrakis(4-alkyl)-phthalocyanines may exist as an isomer mixture. The ability to effect a separation appears to depend, at least partially upon the size of the substituent group. This may well affect the polarity of the final isomers; i.e. a bulky substituent group may cause large differences in polarity between particular isomers and so allow them to be separated by chromatography. Hence it may be possible to separate the phthalocyanine isomers by the use of larger
alkyl groups. This is discussed in more detail later.

No attempt was made in this work to prepare a large number of metal derivatives of these phthalocyanines. Attempts were made only to prepare the nickel complex, although it was assumed that other metal complexes could be made by similar methods.

Attempts to prepare tetrakis(4-n-pentyl)-nickel-phthalocyanine from 4-n-pentyl phthalonitrile and anhydrous nickel chloride, failed. This was presumably due to the thermal decomposition of the dinitrile before the reaction temperature could be reached. However tetrakis-(4-n-pentyl)-nickel-phthalocyanine was prepared by the reaction of tetrakis(4-n-pentyl)-metal free-phthalocyanine with anhydrous nickel chloride in quinoline as solvent. The yield was high and the product was again purified by chromatography on alumina using benzene as eluent.

\[
\text{Experimental}
\]

All analyses given in this section were carried out by Dr. A. Bernhardt, Max Planck Institut für Kohlenforschung, Mühlheim (Ruhr), Germany.
2-n-Pentyl Acrolein

1-Heptanal (redistilled b.p. 153-157°) (128 g), dimethylamine hydrochloride (97.5 g) and formalin (90 g) were heated together at 70° for 24 hours. The mixture was then transferred to a round bottomed flask (1 l) and steam distilled.

The organic layer, of the distillate, was separated, dried over magnesium sulphate and distilled under reduced pressure through a vacuum jacketted column (15 cm, helix packed). The fraction consisting of 2-n-pentyl-acrolein was collected b.p. 69-70° (30 mm; \( \nu^D_{25} 1.4375 \), Lit b.p. 72/30 mm; \( \nu^D_{20} 1.4373 \). Yield 107.4 g (73%).

2-n-Pentyl-3-hydroxy-1-butene

Magnesium turnings (5.3 g) were placed in a flask equipped with a reflux condenser, dropping funnel and a mechanical stirrer. Dry ether (30 ml) was added. A solution of methyl iodide (31.2 g) in dry ether (75 ml) was then added slowly with stirring. The mixture was stirred for a further 20 minutes and then n-pentyl-acrolein (25.3 g) in dry ether (70 ml) was added dropwise. The mixture was allowed to stir for an additional 20 minutes and was then poured on to crushed ice (200 g).

6% Hydrochloric acid (50 ml) was added and the yellow ether solution was separated. The aqueous layer was extracted with ether (4 x 30 ml portions) and the combined extracts were dried over
magnesium sulphate. The ether was removed by distillation and the product was vacuum fractionated. 2-n-pentyl-3-hydroxy-1-butene was collected b.p. 68°/3 mm; n_D^23.5 1.4449; Lit. b.p. 68°/3 mm; n_D^20 1.4448 (55). Yield 22.5 g (79%).

2-n-Pentyl-buta-1,3-diene (Dehydration Method)

2-n-Pentyl-3-hydroxy-1-butene (63.7 g) was added dropwise to a silica column packed with alumina chips (sieve size 6-10), and heated electrically to 240-250°. The drop rate was approximately 1 drop/sec. The issuing gases were condensed and collected in a receiver which was cooled in a dry ice/methanol bath. The reaction was carried out in a slow stream of dry nitrogen. After the reaction had been completed, the organic layer was separated, dried over magnesium sulphate and fractionally distilled through a 15 inch helix packed vacuum jacketed column. The diene fraction was collected b.p. 148-152°, n_D^24 1.4472; Lit. b.p. 148-149° n_D^20 1.4510 (55). Yield 20.0 g (36%).

A higher boiling fraction was collected (b.p. 74-75°/18 mm); which was shown to consist of 3-methyl-octan-2-one. (Lit. b.p. 62-63°/18 mm (65)). The 2,4-dinitrophenylhydrazone and semicarbazone derivatives were prepared by standard methods (66); 2,4-D.N.P. m.p. 56-57° semicarbazone m.p. 98° (65).

2-n-Pentyl-3-acetoxy-1-butene

2-n-Pentyl-3-hydroxy-1-butene (146 g) was heated with acetic
anhydride (309 g) and pyridine (1 ml) on a steam bath for 14 hours. The product was poured on to water (200 ml) and the organic layer was separated. The organic layer was washed with saturated sodium carbonate solution and then with water. It was then dried over anhydrous sodium sulphate. The product was vacuum distilled giving 2-n-pentyl-3-acetoxy-1-butene b.p. 67°/2.3 mm Lit. 78°/4 mm (67).

Yield 168 g (89%).

2-n-Pentyl-buta-1,3-diene (Pyrolysis Method)

The apparatus which was used is represented in Fig. VI. The pyrolysis column was packed with glass balls (4 mm diam.) and was heated, under reduced pressure (120 mm) to 380-400°. The oil bath was slowly heated to 180° while a stream of nitrogen was passed through the apparatus. At this temperature 2-n-pentyl-3-acetoxy-1-butene (160 g) was carried over in the vapour state into the pyrolysis tube. The temperature was measured by means of a thermocouple inserted into a pyrex tube which was sealed at one end, as shown. The pyrosylate was condensed using a coil condenser and finally collected in an acetone/dry ice trap.

The pyrosylate was washed with water (3 x 150 ml) and with 15% sodium hydroxide solution (2 x 150 ml) and was dried over magnesium sulphate. It was fractionated through a 25 cm helix-packed, vacuum jacketted column and the diene fraction b.p. 72-80°/60 mm was collected. A further fraction consisting of recovered acetate was collected.
b.p. 128°/60 mm. The recovered acetate was recycled through the pyrolysis step and the whole process repeated until only a small amount of acetate remained (i.e. 5 pyrolysis cycles).

The diene fractions were combined and refractionation yielded pure 2-n-pentyl-buta-1,3-diene b.p. 70-71°/5.8 mm nD 1.4450;
lit.b.p. 68-69.5/65 mm ? nD 1.4450(67). Yield 28.0 g (31% on unrecovered acetate).

4-n-Pentyl-1,2,3,6-tetrahydrophthalic anhydride

i) 2-n-Pentyl-buta-1,3-diene (22.5 g) was dissolved in acetic acid (90 ml) and maleic anhydride (6.5 g) was added. The mixture was shaken at room temperature for 24 hours and was then added to water (500 ml) and stirred for 24 hours. The white solid was filtered and dried. The white solid consisted mainly of 4-n-pentyl-1,2,3,6-tetrahydrophthalic acid, and it was heated slowly during 1 hour up to its boiling point. It was then distilled under reduced pressure yielding 4-n-pentyl-1,2,3,6-tetrahydrophthalic anhydride b.p. 176-178°/3.5 mm, which solidified upon cooling. Yield 37.5 g (93.2%).

ii) 2-n-Pentyl-buta-1,3-diene (5 g) was dissolved in dry ether (50 ml) and maleic anhydride (6 g) was added. The mixture was heated in a lined autoclave at 50° for 24 hours. Upon cooling the mixture was removed and the ether was allowed to evaporate giving a crystalline residue. 4-n-pentyl-1,2,3,6-tetrahydrophthalic anhydride was
collected and was recrystallised from light petroleum (b.p. 60-80°) as colourless plates m.p. 49-50° Lit. m.p. 49-50°. Yield 8.0 g (90%).

4-n-Pentyl-phthalic anhydride

i) Catalytic Method:- The apparatus used has been described previously (Fig. VII). The reaction vessel was charged with 4-n-pentyl-1,2,3,6-tetrahydrophthalic anhydride (258 mg), 30% palladium on charcoal (prepared as described by Linstead (63)) (240 mg) and naphthalene (1.0 g). The apparatus was purged with CO₂ until no air was left. The reaction vessel was then heated until the naphthalene refluxed vigorously and CO₂ was passed through the apparatus for 6 hours. Little hydrogen gas was collected. The reaction mixture was cooled, dissolved in ether, and the catalyst filtered off. The ether was removed by distillation and the product was stirred with 10% potassium hydroxide solution (20 ml) for 3 hours. The naphthalene was removed by ether extraction and the aqueous solution was acidified. The precipitate was extracted into ether and the ether was removed by distillation. A small amount of residue remained which was 'sublimed' to give one drop of a colourless oil. It was later confirmed as being 4-n-pentyl-phthalic anhydride, by comparison of I.R. spectra.

ii) Oxidative Bromination:- 4-n-Pentyl-1,2,3,6-tetrahydrophthalic anhydride (32.5 g) was dissolved in acetic acid (47 ml) and
heated to 100°. A solution of bromine (62.5 g) in acetic acid (58 ml) was added dropwise over 90 minutes. The mixture was then refluxed for a further 16 hours.

The solvent was removed by rotary evaporation and the black liquid which remained was heated on an oil bath at 180-200° for 10 hours. The black sticky mass which remained was then distilled at high vacuum giving a yellow-green oil. This was redistilled giving 4-n-pentyl-phthalic anhydride as a colourless oil. Yield 25.5 g (80%).

4-n-Pentyl-phthalimide

4-n-Pentyl phthalic anhydride (1 g) was allowed to react with 0.88 ammonia solution (4 ml) and the mixture was slowly heated. The excess ammonia and water were boiled off and the residue was heated to 250°. The mixture solidified on cooling giving 4-n-pentyl-phthalimide as an orange coloured solid. The product was recrystallised from 96% ethanol, m.p. 117°. Yield 0.8 g (80%).

C_{13}H_{15}O_2N \text{ requires } C = 71.86 \text{ H} = 6.96 \text{ N} = 6.45% 

Found \ C = 71.77 \text{ H} = 6.82 \text{ N} = 6.56% 

4-n-Pentyl-phthalamide

4-n-Pentyl phthalamide (300 mg) was shaken with 0.88 ammonia solution (3 ml) and allowed to stand at room temperature for 24 hours. The product was filtered, dried and was recrystallised from ethanol,
m.p. 170°. Yield 264 mg (81.5%).

\[ C_{13}H_{18}O_2N_2 \text{ requires } C = 66.64 \text{ H } = 7.74 \text{ N } = 11.96 \% \]

Found \( C = 66.57 \text{ H } = 7.64 \text{ N } = 11.84 \% \)

**4-n-Pentyl-phthalonitrile**

4-n-Pentyl-phthalamide (10 g) was dissolved in dry pyridine (150 ml) and the mixture heated to 90°. A rapid stream of phosgene was passed through the solution for 90 minutes and the mixture became black and sticky. Crushed ice was carefully added and the product was worked up with water, and acidified with concentrated hydrochloric acid. The dark coloured aqueous solution was extracted continuously with ether (100 ml) for 8 hours. The ether was removed by distillation giving a brown liquid residue. The residue was distilled giving 4-n-pentyl-phthalonitrile as an oil, b.p. 144-149°/0.4 mm.

Yield 6.3 g (74.5%).

\[ C_{13}H_{14}N_2 \text{ requires } C = 78.75 \text{ H } = 7.12 \text{ N } = 14.14 \% \]

Found \( C = 78.64 \text{ H } = 7.06 \text{ N } = 13.94 \% \)

**Tetrakis(4-n-pentyl)-phthalocyanine**

a) Tetrakis(4-n-pentyl)-phthalocyanine-disodium: Sodium metal (190 mg) was allowed to react with 1-pentanol (10 ml) and the mixture was heated under reflux. 4-n-pentyl-phthalonitrile (700 mg) in 1-pentanol (1 ml) was then added and the mixture was refluxed for a further 10 minutes. The green solution was evaporated to dryness giving impure tetrakis(4-n-pentyl)-phthalocyanine-disodium as a green solid.
b) Tetrakis(4-n-pentyl)-phthalocyanine:— The
tetrakis(4-n-pentyl)-phthalocyanine-disodium, prepared above was
refluxed with 50% acetic acid for 2 hours. The product was filtered
off and dried. The crude metal free pigment was dissolved in benzene
and chromatographed on alumina using benzene as eluent. The eluate
was evaporated to dryness and the product was worked up with methanol
in which it was insoluble. Tetrakis(4-n-pentyl)-
phthalocyanine was filtered off as a blue solid with a red lustre.
All attempts to crystallise the compound failed but it could be obtained
analytically pure by chromatography. Yield 360 mg (51%). No m.p.
below 350°C.

\[ \text{C}_{52} \text{H}_{58} \text{N}_8 \text{ requires } \begin{align*} 
C &= 78.55 \quad H = 7.35 \quad N = 14.10 \% \\
\text{Found} &\quad C = 78.74 \quad H = 7.09 \quad N = 14.03 \% 
\end{align*} \]

Tetrakis(4-n-pentyl)-phthalocyanine-nickel

i) Attempts to prepare tetrakis(4-n-pentyl)-phthalocyanine-nickel
from 4-n-pentyl phththalonitrile and nickel chloride, with, or without
a solvent, all failed. This was presumably due to the thermal
instability of 4-n-pentyl-phthalonitrile.

ii) Tetrakis(4-n-pentyl)-phthalocyanine (210 mg)
and anhydrous nickel chloride (200 mg) were refluxed in quinoline
(5 ml) for 90 minutes. The mixture was dissolved in benzene and
washed with 6% hydrochloric acid (4 x 100 ml). The benzene solution
was dried over magnesium sulphate, filtered and the filtrate was
chromatographed on alumina using benzene as eluent. The eluate
was evaporated to dryness and the product worked up with methanol.
Tetrakis(4-n-pentyl)phthalocyanine-nickel was isolated as a blue
solid with a red reflex. Yield 200 mg (8%).

C<sub>52</sub> H<sub>56</sub> N<sub>8</sub> Ni requires C = 73.33 H = 6.63 N = 13.16 %

Found C = 73.51 H = 6.80 N = 13.01 %
C) Tetrakis (3-methyl-4-n-butyl)-phthalocyanines

Tetrakis (4-n-pentyl)-phthalocyanines have been prepared and have been found to have a much enhanced solubility in non-polar solvents. It appeared likely that the peripheral alkyl chains would lower the lattice energy of the solid, and indeed the increased solubility strongly suggests this. Moreover the tetrakis (4-n-pentyl)-phthalocyanines could not be obtained in a crystalline state. The parent phthalocyanines form crystallites very easily, either from their dilute solutions or by the process of sublimation. They are very sparingly soluble and in solution appear, from light absorption studies to exist in an aggregated form. The di-alkoxy-silicon-phthalocyanines, which cannot, of course, form analogous layered molecular aggregates, nevertheless crystallise readily.

Hence, despite the presence of the alkyl chains, the amorphous nature of the tetrakis(4-n-pentyl)-phthalocyanines is rather curious. The possibility arises that the amorphous nature of these compounds is not a direct result of the presence of alkyl chains, but simply that an isomer mixture is present. Proton magnetic resonance studies on these compounds, which are discussed later, also lead to the suspicion that a mixture of isomers may be present.

Sammes, in his work on the tetrakis(3-methyl)-phthalocyanines suggested, from P.M.R. studies that a single isomer was present\(^{(68)}\). It was thought that this might result from a steric effect of the
3-methyl substituent in 3-methyl phthalonitrile causing the
o-phthalic units to unite in a single sense, rather than randomly.
It was felt that an arrangement of the substituents as in the
diagram would therefore be unlikely.

A more probable orientation would be with the methyl groups symmet-
rically distributed:

![Diagram](image)

4- Substituents in phthalonitrile would not however be expected
to exert such a marked directing effect on the course of the nitrile
condensation so that tetrakis(4-n-pentyl)-phthalocyanine would not
be expected to be a single positional isomer.

It seemed that a large group in the 3-position of phthalonitrile
would best direct the condensation to give a single phthalocyanine product. It has been found however that these 3-substituted phthalonitriles are difficult to make.

A possible way of avoiding this difficulty was to employ 3-methyl-4(or 5)-alkyl-phthalonitriles. The small substituent in the 3-position would direct the condensation of the phthalic units so as to give a single pigment isomer. The larger substituent in either the 4- or 5-position would impart enhanced solubility to the product.

Hence the synthesis of tetrakis(3-methyl-4-n-butyl)-phthalocyanine was undertaken. The final product would be an isomer of tetrakis(4-n-pentyl)-phthalocyanine and a comparison of the solubilities would be of interest. The reaction scheme which was used is illustrated below.

**Attempted Preparation of Tetrakis(3-methyl-4-n-butyl)-phthalocyanines**

2-Heptanone was cyanoethylated by the method of Shusherina and coworkers (69), using a large excess of the ketone. 4-Acetyl-octanitrile was isolated by distillation of the reaction mixture. The yield never approached that reported by Shusherina, and even after several repetitions of the preparation was 20% lower.
Acid hydrolysis of the nitrile to 4-acetyl-1-octanoic acid by the literature method (69) was unsatisfactory but alkaline hydrolysis gave considerably improved yields.

\[
\begin{align*}
\text{CH}_3(CH_2)_3 \cdot CH & \quad \text{CH}_2 \\
\text{CH}_3 - C = O & \quad \text{CN} \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3(CH_2)_3 \cdot CH & \quad \text{CH}_2 \\
\text{CH}_3 - C = O & \quad \text{CO}_2\text{H}
\end{align*}
\]

4-Acetyl-1-octanoic acid was isolated by distillation and the 6-enol lactone was prepared by the elimination of water. The method suggested by Shusherina, using acetic anhydride, again proved unsatisfactory and it was found advantageous to use acetyl chloride as dehydrating agent. The yield was thereby much improved, cyclisation taking place to give a reduced 2-pyrone derivative.

\[
\begin{align*}
\text{CH}_3(CH_2)_3 \cdot CH & \quad \text{CH}_2 \\
\text{CH}_3 - C = O & \quad \text{CO}_2\text{H}
\end{align*}
\]

The next stage in the sequence involved oxidative bromination to give the pseudo-aromatic 2-pyrone derivative (70). However the reaction was accompanied by such extensive decomposition that it could only be carried out on a small scale. It had then to be repeated until the required quantity of product was obtained.

Bromination of 5-n-butyl-6-methyl-3,4-dihydro-2-pyrone in ether solution gave the unstable dibromo compound, which was dehydro-
brominated by heating for several hours at 130-140°C. Repeated distillation finally afforded a colourless distillate. A large amount of carbonaceous residue accumulated from these operations.

Attempts were made at allylic bromination of the reduced pyrone using N-bromosuccinimide\(^{(71)}\)

However, these were unsuccessful due to the rapid elimination of hydrogen bromide, when a great deal of charring occurred.

In further attempts to avoid the difficult oxidative bromination step, 4-acetyl-octanoic acid was converted into its acid chloride and attempts were made to \(\alpha\)-brominate this compound\(^{(72)}\).
The intended reaction sequence is shown above. However this method was also unsuccessful due to charring and the original procedure had to be employed.

It was shown by P.M.R. spectroscopy that a large amount of debromination had also taken place upon heating and only about 65% of the distillate consisted of the required aromatic 2-pyrone compound. The latter could not easily be separated from the reduced pyrone by fractional distillation and so it was decided to proceed to the next stage in the reaction sequence with the mixture, assuming it to contain 65% of 5-n-butyl-6-methyl-2-pyrone.

The next stage in the reaction scheme involved the Diels–Alder addition of dimethyl acetylene dicarboxylate to the 5-n-butyl-6-methyl-2-pyrone, and subsequent elimination of carbon dioxide to give 3-methyl-4-n-butyl dimethyl phthalate (73).
Fortunately the diester product could easily be separated from unchanged 5-n-butyl-6-methyl-3,4-dihydro-2-pyrone by distillation.

Attempts were made to convert the diester into the diamide with 0.88 ammonia solution, both at room temperature and at 100° for 12 hours, but no reaction occurred in either case. Even liquid ammonia in methanol at 100° in a sealed tube failed to react with the diester.

An alternative method was then investigated. The diester was hydrolysed to 3-methyl-4-n-butyl phthalic acid, and this was converted into its anhydride.
The anhydride was then converted into its imide by standard methods\(^{(60)}\) and the imide allowed to react with 0.88 ammonia solution. However, no reaction occurred, and neither was the imide converted into the amide when heated with 0.88 ammonia solution at 100° for 10 hours.

It was concluded that the difficulty in the preparation of 3-methyl-4-n-butyl-phthalamid e was due to steric effects. Even though the group in the 3-position was small, the buttressing effect of the group in the 4-position was sufficient to cause severe steric hindrance and prevent the imide ring from opening.

Attempts were made to prepare tetrakis(3-methyl-4-n-butyl)-phthalocyanine copper by the urea melt method\(^{(75)}\). 3-Methyl-4-n-butyl-phthalic anhydride, urea and anhydrous cupric chloride were heated together with a small amount of ammonium molybdate as catalyst, but only traces of a blue pigment could be obtained.
Although there was insufficient for isolation, thin layer chromatography showed that the pigment product was very soluble in non-polar solvents.

Due to the foregoing difficulties, the preparation of 3-methyl-4-n-butyl-phthalonitrile was abandoned. It was still considered of interest to prepare tetrakis(3-methyl-5-n-butyl)-phthalocyanines, and indeed preparation of the required intermediates was likely to be a much better proposition. That particular pigment should be soluble, and would probably be obtained as a single isomer. However lack of time precluded further work in this direction.

Experimental:

Analyses given in this section were carried out by A. Bernhardt, Mulheim (Ruhr), Germany.

4-Acetyl-octanitrile

Acrylonitrile (44.8g) was slowly added to a mixture of 2-heptanone (483g) and 30% methanolic potassium hydroxide solution (6.3ml) so that the temperature remained at 25-30°. The reaction mixture was stirred during the addition and for 2 hours after the addition, at room temperature. The solution was neutralised with concentrated hydrochloric acid (3.3ml), and water (15ml) was added to dissolve the potassium chloride which was precipitated. The organic layer was separated and dried over magnesium sulphate.
The excess 2-heptanone was removed by distillation and the residue distilled giving 4-acetyl-octanitrile b.p. 144-150°/17mm; 
$n_D^{21}$ 1.4420; Lit. b.p. 148-149°/18mm; $n_D^{20}$ 1.4425(69). Yield 53.6g (38%).

4-Acetyl-octanoic acid

4-Acetyl-octanitrile (40g) was refluxed with a solution of sodium hydroxide (12g) in water (40ml) for 3 hours. The solution was acidified and the acid which was liberated was extracted into ether. The ethereal layer was separated and the aqueous solution was extracted with ether (3 x 40ml). The mixed ether extracts were dried over magnesium sulphate and the ether was removed by distillation. The residue was distilled under reduced pressure, and 4-acetyl-1-octanoic acid was collected b.p. 157-160°/4mm; 
$n_D^{22}$ 1.4496; Lit. b.p. 165-167°/6mm; $n_D^{20}$ 1.4504(69). Yield 33g (74%).

5-n-Butyl-6-methyl-3,4-dihydro-2-pyrene

4-Acetyl-1-octanoic acid (33g) and acetyl chloride (165g) were refluxed together for 5 hours. The excess acid chloride was removed by distillation, and the residue was distilled under reduced pressure. 5-n-Butyl-6-methyl-3,4-dihydro-2-pyrene was collected b.p. 127-131°/3mm; $n_D^{20}$ 1.4680; Lit. b.p. 126-127°/10mm; $n_D^{20}$ 1.4673(69). Yield 26.0g (87%).
5-n-Butyl-6-methyl-2-pyrone

5-n-Butyl-6-methyl-3,4-dihydro-2-pyrone (25g) was dissolved in dry ether (25ml), and bromine (24g) was added dropwise with shaking while the mixture was cooled in an ice/salt bath. The ether was then removed by bubbling a stream of dry air through the mixture. The residue, consisting of the dibromo-compound, was then slowly heated up to 140° during 4 hours, under reduced pressure. A stream of nitrogen was slowly bubbled through the mixture during the period of heating. The liquid material was then completely distilled from the reaction mixture and collected as a dark coloured oil. The oil was redistilled until a stable colourless oil was obtained.

The procedure was repeated in 25g batches until a total of 69g of reduced pyrone had been used. The total distillates were then combined and redistilled. The fraction b.p. 110-120°/2mm, (30g), was collected, and was shown by P.M.R. spectroscopy to contain 65% of 5-n-butyl-6-methyl-2-pyrone. Yield of 5-n-butyl-6-methyl-2-pyrone, 20g (32% on unrecovered 5-n-butyl-6-methyl-3,4-dihydro-2-pyrone).

3-Methyl-4-n-butyl dimethyl phthalate

5-n-Butyl-6-methyl-2-pyrone (30g) containing about 35% of its dihydro-derivative was heated with dimethyl acetylene dicarboxylate (20g), to 140°. The temperature was then slowly raised to
180-190°, and carbon dioxide was evolved. The temperature was maintained at 180-190° for a further 2 hours, until the evolution of carbon dioxide had ceased. The product was then vacuum fractionated when the diester could be separated easily from recovered 5-n-buty1-6-methyl-3,4-dihydro-2-pyrone. 3-Methyl-4-n-butyl dimethyl phthalate was collected b.p. 162-166°/2mm; nD^25 1.5123. Yield 22g (71%).

C_{15}H_{20}O_4 requires C = 68.16, H = 7.63%
Found C = 68.08, H = 7.60%

3-Methyl-4-n-butyl-phthalamide

a) 3-Methyl-4-n-butyl dimethyl phthalate (720mg) was shaken for 3 days with 0.88 ammonia solution (4ml) and a trace of methanol as cosolvent. No solid amide could be isolated. The oily residue was found, by I.R. spectroscopy, to consist of unchanged dimethyl ester.

b) 3-Methyl-4-n-butyl dimethyl phthalate (2.0g) was mixed with 0.88 ammonia solution (5ml), and methanol (2ml) was added as a cosolvent. The mixture was sealed in a Carius tube and heated at 100° for 12 hours. 3-Methyl-4-n-butyl dimethyl phthalate was recovered unchanged, but impure, when the solvent was removed by evaporation.

c) 3-Methyl-4-n-butyl dimethyl phthalate (2.0g) was dissolved in
methanol (5ml) in a Carius tube. Liquid Ammonia (3ml) was added and the tube was sealed. It was heated for 8 hours at 100°. When the solvent was evaporated, the residue was shown, by I.R. spectroscopy to consist of unchanged dimethyl ester.

3-Methyl-4-n-butyl phthalic acid

3-Methyl-4-n-butyl dimethyl phthalate (1.3g) was refluxed with 20% ethanolic potassium hydroxide solution (7ml) for 2 hours. Water (3ml) was added and refluxing was continued for a further 60 minutes. The alcohol was removed by distillation and the solution was acidified with hydrochloric acid. The acid which was precipitated, was filtered off and was dried in a vacuum desiccator. 3-Methyl-4-n-butyl phthalic acid was recrystallised from water m.p. 150-151°; Lit. m.p. 157-158°(73). Yield 11g (95%).

3-Methyl-4-n-butyl phthalic anhydride

3-Methyl-4-n-butyl phthalic acid (500mg) was heated on a steam bath with acetyl chloride (22.5ml) for 1 hour. The excess acetyl chloride was removed by distillation. The residual oil was sublimed under high vacuum to give crystalline 3-methyl-4-n-butyl phthalic anhydride m.p. 35°; Lit. m.p. 37°(73). Yield 345mg (75%).

3-Methyl-4-n-butyl phthalimide

3-Methyl-4-n-butyl phthalic anhydride (500mg) was allowed to react with 0.88 ammonia solution (1.5ml) and the excess ammonia
and water were removed by boiling the solution. The residue was heated to 300° during 30 minutes, and then allowed to cool. 3-Methyl-4-n-butyl phthalimide crystallised as a solid mass. It was recrystallised from aqueous methanol m.p. 168°. Yield 342mg (68%).

\[ C_{13}H_{15} \text{NO}_2 \text{ requires } C = 71.86, \; H = 6.96, \; N = 6.45 \% \]

\[ \text{Found } C = 72.04, \; H = 7.16, \; N = 6.51 \% \]

**Tetrakis(3-methyl-4-n-butyl)-phthalocyanine-copper**

3-Methyl-4-n-butyl phthalic anhydride (96mg), uroa (187mg) and a few milligrammes of ammonium molybdate were heated in trichlorobenzene, at reflux for 2 hours. The solvent was removed by steam distillation and the solid was filtered off. The solid was washed with dilute hydrochloric acid and then with water, and was extracted into chloroform. A small amount of blue pigment was formed but was insufficient for isolation. Thin layer chromatography indicated that the compound was not very polar and was very soluble in the chloroform eluate.
D) Tetrakis(4-t-butyl)-phthalocyanines

Although the tetrakis(3-methyl-4-n-butyl)-phthalocyanines appeared to be very difficult to prepare, indications had been obtained to show that they were very soluble in chloroform. If the methyl group contributed little to this property then it was concluded that the four butyl groups around the periphery of the ring were mainly responsible.

Whilst it had been shown that straight alkyl chains attached to the periphery of the phthalocyanine molecule imparted greatly enhanced solubility, it was also apparent that this type of substituent contained many non-equivalent hydrogen atoms and so would give rise to complicated P.M.R. spectra. Indeed no sharp signals could be observed in the P.M.R. spectra of any of the tetra-(alkyl)-phthalocyanines so far described. (The P.M.R. studies are discussed later). The number of chemically equivalent hydrogen atoms could be increased, without any decrease in chain length, by making use of chain branching.

Hence t-butyl was used as a solubilising group instead of n-butyl, the substitution again being made in the 4-position for reasons already discussed. The advantages of this grouping over others so far as P.M.R. spectroscopy is concerned, are twofold.

1) Since 9 equivalent protons are present in each t-butyl group, strong signals will result and relatively dilute solutions of the
phthalocyanine can be used.

ii) If more than one t-butyl signal were observed, then information concerning positional isomerism would be forthcoming.

It was also expected that tetrakis(4-t-butyl)-phthalocyanine would have a higher solubility than its straight chain isomer because of the increased bulk of the group, which would interfere with, or prevent, molecular stacking.

The synthesis of the 4-t-butyl phthalonitrile precursor proved considerably easier than any of the 4-alkyl phthalonitriles so far discussed.

The Synthesis of 4-t-butyl-phthalonitrile

The synthesis was based on work by A.T. Peters(76). The route makes use of the special properties of the tertiary butyl group. A Friedel-Craft's alkylation was used to introduce this group into o-xylene, which was then selectively oxidised to the phthalic acid derivative.

t-Butyl chloride, prepared by the reaction of t-butanol with concentrated hydrochloric acid(77), was allowed to react with o-xylene in the presence of anhydrous ferric chloride(76). The alkylation proceeded vigorously at room temperature with the liberation of hydrogen chloride and exclusive production of 4-t-butyl-1,2-dimethyl-benzene.
The 4-t-butyl-1,2-dimethyl benzene was selectively oxidised with potassium permanganate in aqueous pyridine, and the phthalic acid isolated after addition of concentrated hydrochloric acid.

The 4-t-butyl phthalic acid was converted, with acetic anhydride, into its anhydride, a very vigorous process, and the 4-t-butyl phthalic anhydride was isolated by distillation at 300-315°C. This was the best method of isolation. The anhydride was treated with 0.88 ammonia solution, the solvent evaporated off and the mixture strongly heated to 300°C when 4-t-butyl-phthalimide was formed (60).

The 4-t-butyl-phthalimide, unlike 3-methyl-4-n-butyl-phthalimide reacted readily with 0.88 ammonia solution to form 4-t-butyl-phthalanide (61).
The diamide was dehydrated by bubbling a rapid stream of phosgene through a pyridine solution of the diamide, at 90-100°C(62). 4-t-Butyl phthalonitrile was then isolated as a white highly crystalline solid.

Tetrakis(4-t-butyl)-phthalocyanines

As in the case of the tetrakis(4-n-pentyl)-phthalocyanines, no attempt was made to prepare a large number of metallated derivatives. Only the nickel complex was made, and it was assumed that other metal derivatives could be made by similar methods.

Tetrakis(4-t-butyl)-phthalocyanine was prepared by demetallation with 50% acetic acid of the disodium derivative, prepared by standard methods(17), and was purified by chromatography on alumina (Brockman activity 2), using benzene as eluent. The benzene was removed by evaporation and the product isolated by treatment with methanol in which it was insoluble. The pigment, as in the case of tetrakis(4-n-pentyl)-phthalocyanine could not be obtained in a crystalline state. However, it was obtained analytically pure from the
chromatography column.

It is possible that a number of isomers may be present but no evidence for this has been found from chromatographic studies.

Metallated phthalocyanines which have been prepared include the nickel and dichloro-tin derivatives. The tin compounds are reported separately in Section IV. Tetrakis(4-t-butyl)-phthalocyanine-nickel was prepared by the urea melt method, using 4-t-butyl-phthalic anhydride, anhydrous nickel chloride, urea and ammonium molybdate as catalyst\(^7\). The copper complex was also prepared by this method but the yield tended to be rather low and the product was somewhat impure. Chromatography used to purify the metallated phthalocyanines.

Tetrakis(4-t-butyl)-phthalocyanine-nickel was also obtained by the reaction of molten 4-t-butyl-phthalonitrile with anhydrous nickel chloride. It was shown that 4-t-butyl phthalonitrile is much less reactive than phthalonitrile under these conditions. Very long reaction times and high temperatures were needed to produce any pigment and even then the yields were low. Tetrakis (4-t-butyl)-phthalocyanine-iron II was also prepared by the reaction of ferric acetate with 4-t-butyl-phthalonitrile, but the yield was
very low. The dicyanoferrate II complex was also prepared by reaction with potassium cyanide in methanol\(^{(79)}\).

\[
\begin{array}{cc}
\text{Fe} & \text{CN} \\
\text{Fe} & \text{CN} \\
\end{array}
\quad \Rightarrow \quad
\begin{array}{cc}
\text{Fe} & \text{CN} \\
\text{Fe} & \text{CN} \\
\end{array}
\quad 2K^+ 
\]

This compound was very soluble in methanol and its P.M.R. spectrum was obtained in this solvent. The spectrum is discussed later.

It is suggested from work on the metallated tetrakis(4-n-pentyl)-phthalocyanines that the best method for preparing metal derivatives of the tetrakis(4-alkyl)-phthalocyanines is to use the metal free derivative as precursor. The reaction times needed are short and the yields tended to be very high. The reaction is best carried in quinoline, as solvent, at reflux. The quinoline is then removed by washing with acid and the product is easily purified by chromatography, to give the pigment in almost quantitative yield and in a highly pure state.

Experimental

All analyses were carried out by A. Bernhardt, Mulheim (Ruhr), Germany.

t-Butyl chloride

t-Butanol (400g) was placed in a 3 litre separatory funnel and concentrated hydrochloric acid (1350ml) was carefully added. The
mixture was shaken for about 5 minutes and the two layers were allowed to separate. The organic layer was washed with saturated sodium bicarbonate solution (500ml) and then with water (2 x 500ml). It was dried over anhydrous calcium chloride and distilled. t-Butyl chloride was collected b.p. 50-51.5°; Lit. 49.5-52°(77). Yield 416.5g (83%).

4-t-Butyl-1,2-dimethyl-benzene

o-Xylene (300g) and t-butyl chloride (262g) were stirred together and anhydrous ferric chloride (2.5g) was added slowly over 30 minutes, at room temperature. A vigorous evolution of hydrogen chloride occurred, and when it had eventually subsided, more t-butyl chloride (55g) was added. The mixture was stirred for a further hour and was heated on a steam bath for 15 minutes. It was filtered through charcoal and the filtrate was vacuum fractionated. 4-t-Butyl-1,2-dimethyl-benzene was collected b.p. 124-126°/42mm; nD 1.4985; Lit. b.p. 211-212°; nD 1.5002(75). Yield 357g (78%).

4-t-Butyl-phthalic anhydride

4-t-Butyl-1,2-dimethyl-benzene (81g) was dissolved in pyridine (500ml) and water (1000ml) was added. The mixture was stirred and heated to reflux in a 3 litre 3 necked flask. When the mixture had begun to boil, potassium permanganate (360g) was carefully added over 90 minutes. External heating was discontinued as the exothermic
reaction kept the solution at reflux during the addition. After the addition, the mixture was again heated at reflux for a further 30 minutes. The excess permanganate was then destroyed by addition of ethanol, and the mixture was filtered. The manganese dioxide was washed well with several litres of hot water and the filtrate and washings were combined. The solution was concentrated to 300ml and then cooled in an ice bath. It was carefully acidified until it was just acidic (pH : 3) and the white solid which was precipitated was filtered off. (N.B. The acidification was very critical, as the solid became very sticky if the solution became too acidic.) The white solid, consisting of the mono-potassium salt of 4-t-butyl-phthalic acid, was stirred with concentrated hydrochloric acid overnight. The solid, which then consisted of a mixture of 4-t-butyl phthalic acid and potassium chloride was filtered off, and dried.

The dry solid was heated to reflux for 1 hour with acetic anhydride, when a vigorous reaction took place. The phthalic derivative dissolved as the anhydride and potassium chloride remained in suspension. Potassium chloride was filtered off, and the filtrate was distilled. Excess acetic anhydride was removed and the residue was distilled at atmospheric pressure. 4-t-Butyl-phthalic anhydride was collected b.p. 300-315° as a pale yellow oil which solidified upon standing. (N.B. This method was found to have considerable practical advantages over either vacuum distillation,
4-t-Butyl-phthalic anhydride was recrystallised from light petroleum (b.p. 60-80°), m.p. 77°; Lit. m.p. 77°(76). Yield 60g (59%).

4-t-Butyl-phthalimide

4-t-Butyl phthalic anhydride (4.3g) was allowed to react with 0.88 ammonia solution (15ml). The excess ammonia and water were removed by boiling and the residue was heated to 280°, and then allowed to cool. The mixture solidified as a brownish mass. 4-t-Butyl phthalimide was recrystallised from ethanol m.p. 134°; Lit. m.p. 133-134°(76). Yield 4.3g (100%).

4-t-Butyl-phthalamide

4-t-Butyl-phthalamide (500mg) was stirred with 0.88 ammonia solution (5ml) for 3½ hours at room temperature. The diamide was filtered off as a white solid and dried under vacuum. 4-t-Butyl-phthalamide was recrystallised from water, with a little ethanol, as needles m.p. 165°. Yield 460mg (85%).

\[
\begin{align*}
C_{12}H_{16}O_2N_2 & \text{ requires } C = 65.44 \quad H = 7.32 \quad N = 12.71 \% \\
\text{Found} & \quad C = 65.53 \quad H = 7.52 \quad N = 12.54 \%
\end{align*}
\]

4-t-Butyl-phthalonitrile

4-t-Butyl phthalamide (21g) and dry pyridine (325ml) were heated, in a 1 litre reaction vessel, to 60°. A rapid stream of phosgene
was passed through the solution and the temperature rose to 90°. The reaction mixture became black and very viscous. Phosgene was passed through the mixture for 90 minutes, and then it was worked up with crushed ice and finally with water. It was acidified with concentrated hydrochloric acid, and the black mixture was extracted continuously with ether for 6 hours. The ether was removed by distillation leaving an oil, which solidified upon cooling. Recrystallisation of the solid from methanol, using decolourising charcoal, yielded 4-t-butyl-phthalonitrile m.p. 59°. Yield 14.3g (86%).

\[
\text{C}_{12}\text{H}_{12}\text{N}_2 \quad \text{requires} \quad C = 78.23 \quad H = 6.57 \quad N = 15.20 \%
\]

\[
\text{Found} \quad C = 78.33 \quad H = 6.30 \quad N = 15.26 \%
\]

**Tetrakis(4-t-butyl)-phthalocyanine**

a) **Tetrakis(4-t-butyl)-phthalocyanine-disodium**: Sodium metal (0.28g) was allowed to react with 1-pentanol (10ml) and the solution was heated to reflux. 4-t-Butyl-phthalonitrile (1.0g) was added and refluxing was continued for a further 15 minutes. The alcohol was removed on a rotary evaporator leaving a green solid residue of tetrakis(4-t-butyl)-phthalocyanine-disodium.

b) **Tetrakis(4-t-butyl)-phthalocyanine**: Tetrakis(4-t-butyl)-phthalocyanine-disodium, prepared as above, was refluxed with 50% acetic acid (15ml) overnight and the mixture was filtered. The solid was dried and was dissolved in dry benzene. It was chromatographed
on alumina using benzene as eluent, and the fast moving blue band
was collected. The eluate was evaporated to dryness, and the
solid residue was worked up with methanol. Tetrakis(4-t-butyl)-
phthalocyanine was collected as a blue solid with a rich red lustre.
The solid was dried under vacuum. Yield 490 mg (49\%).

\[ C_{48}H_{50}N_8 \text{ requires } C = 78.00 \quad H = 6.82 \quad N = 15.17 \%
\]

\[ \text{Found } C = 78.01 \quad H = 6.91 \quad N = 15.08 \%
\]

**Tetrakis(4-t-butyl)-phthalocyanine-nickel**

i) 4-t-Butyl-phthalic anhydride (2.1 g), urea (6.0 g), and ammonium
molybdate (50 mg) were heated with anhydrous nickel chloride (440 mg)
in nitrobenzene (17.5 ml) at 200° for 3 hours. The reaction mixture
was steam distilled until all traces of the solvent had been removed.
The hot aqueous suspension was filtered, washed with dilute hydro-
chloric acid, dilute sodium hydroxide solution, and then with water.
The residue was dried and was extracted with benzene. The benzene
solution was chromatographed on alumina using benzene as eluent.
The fast moving blue band was collected and evaporated to dryness.
The residue was worked up with methanol according to the usual
procedure. Tetrakis(4-t-butyl)-phthalocyanine-nickel was collected
and dried. Yield 520 mg (25\%).

ii) 4-t-Butyl-phthalonitrile (1.0 g) was heated with anhydrous
nickel chloride (600 mg) at 280-290° for 8 hours. The mixture became
solid, and was allowed to cool. It was extracted with benzene, and
the benzene solution was chromatographed on alumina using benzene as eluent. The fast moving blue band was collected and the eluate was evaporated to dryness. The solid which was deposited was worked up with methanol. Tetrakis(4-t-butyl)-phthalocyanine-nickel was collected by filtration, and was dried under vacuum. Yield 314mg (29%).

\[
\text{C}_{48}\text{H}_{48}\text{N}_8\text{Ni requires } C = 72.46 \quad H = 6.08 \quad N = 14.08 \%
\]

\[
\text{Found } C = 71.59 \quad H = 6.59 \quad N = 13.73 \%
\]

**Tetrakis(4-t-butyl)-phthalocyanine-iron(II)**

4-t-Butyl-phthalonitrile (1.0g) was heated with ferric acetate at 290° for 7 hours. Upon cooling, the mass was dissolved in dry benzene and filtered. The filtrate was chromatographed on alumina using benzene as eluent. The fast moving blue band was collected and evaporated almost to dryness. The pigment was precipitated by the addition of absolute ethanol, and dried under vacuum. Yield 25mg (2.3%).

**Dipotassium tetrakis(4-t-butyl)-phthalocyanine-dicyanoferrate(II)**

Potassium cyanide (12.5mg) in absolute ethanol (1.2ml) was warmed, and tetrakis(4-t-butyl)-phthalocyanine-iron(II) (25mg) was added. The mixture was refluxed for 48 hours and was diluted with methanol (2ml) and filtered. The filtrate was evaporated to dryness, and the product was again dissolved in methanol. It was
again filtered and the procedure repeated. The compound could not be isolated\(^{(23)}\) due to decomposition but its P.M.R. spectrum was obtained in methanolic solution.
E) Discussion and Proton Magnetic Resonance Studies

i) Discussion

Tetrakis(4-alkyl)-phthalocyanines have been prepared where the alkyl group has four or five carbon atoms. The solubility of these macrocycles, in chloroform, has been shown to be remarkably high, in fact it appears to be greater than the solubility of the di-alkoxy-silicon-phthalocyanines. Attempts to determine the absolute solubility of these compounds failed because insufficient material was available. However, it was shown that the solubility of both tetrakis(4-n-pentyl)- and tetrakis(4-t-butyl)-phthalocyanines was higher than 15% w/w in cold chloroform. The solubility of these compounds in polar solvents such as methanol or ethanol is very low, considerably lower in fact than that of the di-alkoxy-silicon-phthalocyanines. This illustrates that the tetrakis(4-alkyl)-phthalocyanines tend to be less polar than the di-alkoxy-silicon-phthalocyanines, as might be expected. As a result of the decrease in polarity, it has been shown that the tetrakis(4-alkyl)-phthalocyanines tend to be relatively easy to purify by column chromatography. The purification of di-alkoxy-silicon-phthalocyanines necessitates the use of deactivated alumina, but with tetrakis(4-alkyl)-phthalocyanines, this need not be used. It has been shown that the use of substrates such as anhydrous sodium sulphate, and cellulose powder are unsuitable for the purification of these macrocycles, because the more polar impurities tend to pass down the column.
There appears to be no reason why a symmetrical isomer should be formed preferentially in the preparation of tetrakis(4-alkyl)-phthalocyanines, and hence a mixture of all possible arrangements would be expected. Four isomers are possible, and these are represented in Fig. VIII.

![Diagram of isomers A, B, C, D](image)

Fig. VIII

No separation of the material by thin layer, or column chromatography was effected and so no evidence for the presence of positional isomers is yet available. A synthesis has been devised whereby a symmetrical isomer should be obtained exclusively. This involves the stepwise preparation of the macrocycle (80); and the synthesis is summarised in Fig. IX. Unfortunately the synthesis was not completed, principally due to lack of time, but it appeared to hold some promise. Compounds I and II (Fig. IX) have been prepared and it appeared from the P.M.R. spectrum of II that the alkyl
substituent was in the 5-(or 6-) position exclusively. (N.B. The exact position of the t-butyl group was not known but it is not important as either substitution would lead to the same macrocycle.) The t-butyl signal of 5(or 6)-t-butyl-1-imino-3-phenylimino-isoindoline (II) appeared as a sharp singlet.

ii) Proton Magnetic Resonance Studies

The solubility of the tetrakis(4-alkyl)-phthalocyanines in chloroform has been shown to be remarkably high and so these compounds were apparently very suitable for P.M.R. studies.

Tetrakis(4-n-pentyl)-phthalocyanines

The P.M.R. spectrum of tetrakis(4-n-pentyl)-phthalocyanines in deuteriochloroform solvent, proved to be rather disappointing. The spectrum consisted of a series of broad bands (Fig. Xa). An interesting feature of the spectrum however was the 2 proton peak at 14.7T. This was assigned to the central N-H protons of the metal free compound, which suffer a high degree of shielding since they are in the centre of the aromatic macrocycle.

The P.M.R. spectrum of tetrakis(4-n-pentyl)-phthalocyanine-nickel has also been obtained in deuteriochloroform solution. The chemical shifts associated with the aromatic and aliphatic protons of the two compounds are listed in Table VII.
Fig X

(a)

(b)
From these results it can be concluded that the ring current sustained by the metal free derivative is greater than that of the metallated compound. The reason for this may be a "short circuiting" effect across the ring due to the presence of the central nickel atom. Hence the induced magnetic field would be less in the case of the metal derivative and the deshielding of the peripheral protons would be reduced. It can be seen that the A, B and X protons associated with the aromatic ring appeared to considerably higher field in the case of the nickel complex than in the metal free compound. A similar observation was made for the protons of the n-pentyl chain on the periphery of the ring. The effect can be seen to decrease as the distance from the centre of the ring increased, as would be expected on theoretical grounds.

**Tetrakis(4-t-butyl)-phthalocyanines**

Proton magnetic resonance studies have been carried out upon
the tetrakis(4-t-buty1)-phthalocyanines and as expected have proved
of more interest than those with the n-pentyl chains. The spectrum
of tetrakis(4-t-buty1)-phthalocyanine is shown in Fig. Xb. The
spectrum was again quite complex and an interesting feature was the
central N-H protons which were again very highly shielded, and
appeared at 14.0T. The aromatic region of the spectrum was again
broadened and little fine structure could be observed. However,
comparison of the metal free, and nickel complexes showed a similar
effect to that found in the n-pentyl case. The aromatic protons
in the metal free derivative appeared at considerably lower field
than in the metallated compound, again showing the greater aromatic
character of tetrakis(4-t-buty1)-phthalocyanine over tetrakis(4-
t-buty1)-phthalocyanine-nickel. This was further demonstrated by
the fact that the t-buty1 signals associated with the metal free
derivative appeared some 0.1 p.p.m. to lower field than in the
nickel compound.

The line broadening and abnormal splitting associated with the
aromatic and aliphatic protons of the n-pentyl and t-buty1 deriva-
tives made accurate measurement of chemical shifts difficult and
hence made accurate deductions as to the aromaticities difficult.
An explanation for the broadening of the bands became apparent upon
studying the t-buty1 signal in the tetrakis(4-t-buty1)-phthalocyanine
complexes. The t-buty1 signal appeared as a complex multiplet of
sharp peaks, and not as was expected, a sharp singlet. This was the
first indication that a mixture of positional isomers may be present. The t-butyl groups of the different isomers would be in different chemical environments, and would hence come to resonance at a slightly different field from each other. Hence a multiplet of sharp peaks would be expected. From these results it was initially concluded that a mixture of isomers were present. Single isomers could to some extent be identified by the multiplicity of the t-butyl signals. Hence considering the isomers represented in Fig. VIII, 'A' would give rise to a singlet; 'B' to a singlet; 'C' to a doublet and 'D' to a quartet, for the t-butyl signals.

This conclusion however conflicts with work carried out by Sammes. He observed a singlet for the methyl group in the P.M.R. spectrum of dipotassium tetrakis(4-methyl)-phthalocyanine-dicyanoferrate (II) in methanol. If a mixture of isomers were present in this case, then the same multiplicity in the signal would be expected as indicated for the tetrakis(4-t-butyl) compounds.

In order to clarify the situation, dipotassium tetrakis(4-t-butyl)-phthalocyanine-dicyanoferrate (II) was prepared and the P.M.R. spectrum was obtained in methanol as solvent. The result was in complete agreement with that of Sammes. The t-butyl group appeared as a sharp singlet. Furthermore the aromatic region of the spectrum appeared to be resolved. The chemical shifts of the aromatic protons compared with those of the system reported by Sammes were of course different but the general appearance of this region of the
spectrum, (i.e. the splitting pattern) was essentially similar.

The aromatic part of the spectrum was split into two distinct regions as for an ABX pattern. The $H_x$ proton appeared as a double doublet centred at 2.06 T and the $H_A$ and $H_B$ protons appeared together as a multiplet, from 0.63 T to 1.02 T. The t-butyl group appeared as a sharp singlet at 8.27 T.

It is difficult to compare these results directly with those of the metal free and nickel derivatives, since completely different solvents were used and comparison of chemical shifts would be meaningless. However the fact that the P.M.R. spectrum of the phthalocyanine-dicyanoferrate complex appeared highly resolved, introduced a problem with regard to the spectra of metal free and nickel complexes where splitting of peaks occurred. It was concluded that this splitting cannot be explained by any of the arguments so far put forward.

Discussion of P.M.R. Data

Abraham and his coworkers\textsuperscript{81} have observed abnormal splitting of peaks in the porphyrin series, and this has been attributed to concentration effects. Abraham assumed that a two unit species
existed in solution (i.e. two unit aggregates) in which the two component macrocycles were associated parallel to each other. He suggested that each caused shielding of the other to differing degrees at points around the ring, due to the shape of the macrocycle. Hence signals appeared to be split as a result of the diamagnetic anisotropy of the rings. A similar effect is believed to occur in the case of phthalocyanine. However, it seems more likely that the effect is simply one of aggregation of molecules in concentrated, rather than the existence of specific bimolecular or trimolecular units. This has been shown to be the case.
P.M.R. spectra have been obtained of the tetrakis(4-n-pentyl) and tetrakis(4-t-butyl)-phthalocyanines at various concentrations from 10% down to 0.5% w/w in deuteriochloroform. It has been shown that under dilute solution conditions the t-butyl signal of tetrakis(4-t-butyl)-phthalocyanine appeared to collapse to a singlet (Fig. XI). Unfortunately, at the highest dilutions the aromatic region of the spectrum was lost in background noise.

If the effect were simply one of molecular aggregation however then staggered aggregation similar to that observed in the crystal lattice might have been expected (Fig. I). This would presumably be the most stable arrangement. However this type of aggregation would involve the periphery of a ring experiencing a high degree of shielding since it would be close to the centre of the adjacent macrocycle.
Fig XI

CONCENTRATION (w/w)

0.48%  2.14%  4.63%  10.28%
Fig XII

- N-H PROTONS OF TETRAKIS(4-t-BUTYL)PHTHALOCYANINE
- N-H PROTONS OF TETRAKIS(4-n-PENTYL)PHTHALOCYANINE
- O-CH₃ PROTONS OF BIS(METHOXY)-SILICON-
  TETRAKIS(4-t-BUTYL)-PHTHALOCYANINE

CONCENTRATION (%v/w) ----

---

CONCENTRATION (%w/w) ----
It has been found that this is not so, and in fact the central N-H protons suffer the greatest change in chemical shift upon dilution of the solution (Fig. XII), while the peripherally substituted t-butyl groups appear to suffer little or no change in chemical shift. The observed effect has been explained in terms of the orientation of the macrocycles caused by the applied magnetic field.

It seems that the applied field causes orientation of the molecules. The induced magnetic field causes the molecules to act as minute bar magnets as shown in Fig. XIII and hence the aggregates tend to be stacked as shown and not staggered as in the case of the molecular aggregates in the crystal. This hypothesis would explain the results where a high degree of concentration dependence is shown.
by the central N-H protons and little effect on the periphery of the ring.

The fact that the dicyanoferrate complexes do not appear to suffer the effect of aggregation can be explained using the above argument. The cyano groups, being coordinated to the iron atom on both sides of the phthalocyanine ring tend to prevent the molecules approaching sufficiently close to cause aggregation in concentrated solution. As a result the intermolecular shielding effects are not observable in these compounds. According to this theory the chemical shifts of the protons associated with the dicyanoferrate complex should not be concentration dependant but no experiments have been carried out to prove this.

This theory can also be used to explain why no abnormal splittings due to concentration effects were observed in the case of the 'di-alkoxy-silicon-phthalocyanines. It appears that the long alkoxy chains were sufficiently bulky to prevent aggregation of the molecules in the concentrated solution used in P.M.R. spectroscopy.

iii) Conclusion

It has not been possible to study the tetrakis(4-alkyl)-phthalocyanines completely due to aggregation effects in solution. At very low concentration however when aggregation would be minimal, the aromatic region of the spectrum could not be observed because of "background noise". It may be possible, using a time averaging
computer to eliminate this "noise" and obtain spectra in very dilute solution.

It has been shown that the splitting of the t-butyl group in the P.M.R. spectra of the tetrakis(4-butyl)-phthalocyanines is not, as was first supposed, due to the slightly different chemical shift of positional isomers. It has been shown that at high dilution, this t-butyl splitting disappeared. However, this does not eliminate the possibility that the compounds exist as an isomer mixture. The most promising approach to this problem appears to lie in the elective synthesis of a specific isomer of the substituted macrocycle. There is room for considerably more work in this field.
DI-ALKOXY-SILICON-TETRAKIS(4-ALKYL)-PHTHALOCYANINES

A) Di-alkoxy-silicon-tetrakis(4-alkyl)-phthalocyanine compounds

i) Introduction: Two kinds of phthalocyanine derivative, namely the tetrakis(4-alkyl)-phthalocyanines and the di-alkoxy-silicon-phthalocyanines have been found to be very soluble in non-polar solvents. (Sections I and II).

The P.M.R. spectra of the tetrakis(4-alkyl)-phthalocyanines were not straightforward, being complicated by effects arising from molecular aggregation. However, no similar difficulties were encountered with the di-alkoxy-silicon-phthalocyanines. The reason appears to be that the long alkoxy chains prevent close approach of molecules in concentrated solution.

If this hypothesis is correct, then it is expected that the tetrakis(4-alkyl)-phthalocyanine macrocycles could be studied through their di-alkoxy-silicon complexes. Accordingly, a number of di-alkoxy-silicon-tetrakis(4-alkyl)-phthalocyanines have been prepared, and are described in this section.

A further reason for the preparation of di-alkoxy-silicon-tetrakis(4-alkyl)-phthalocyanines was to study the melting point of these compounds.

Although the tetrakis(4-alkyl)-phthalocyanines had no melting point below $350^\circ$, many of the intermediates in their synthesis were
found to have considerably lower melting point than the corresponding unsubstituted derivatives. Some observations are recorded in Table VIII. In certain cases, compounds which were solids when unsubstituted, were obtained as liquids when an alkyl group was substituted in the 4-position of the benzene ring, despite the increase in molecular weight. These observations help to confirm the theory that the introduction of a bulky group was responsible for the decrease in crystal stability and consequent lowering of melting point.

<table>
<thead>
<tr>
<th></th>
<th>UNSUBSTITUTED</th>
<th>4-t-BUTYL SUBSTITUTED</th>
<th>4-n-PENTYL SUBSTITUTED</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phthalic Anhydride</td>
<td>132°</td>
<td>77°</td>
<td>liquid</td>
</tr>
<tr>
<td>Phthalimide</td>
<td>238°</td>
<td>134°</td>
<td>117°</td>
</tr>
<tr>
<td>Phthalamide</td>
<td>219-220°</td>
<td>165°</td>
<td>166-167°</td>
</tr>
<tr>
<td>Phthalonitrile</td>
<td>141°</td>
<td>59°</td>
<td>liquid</td>
</tr>
</tbody>
</table>

**TABLE VIII**

It was expected that the melting point of the di-alkoxy-silicon-phthalocyanines would be further lowered by the substitution of alkyl groups around the periphery of the ring.

ii) **Discussion:** 5-n-Pentyl-1,3-diiminoisoindoline was prepared by the reaction of 4-n-pentyl phthalonitrile with liquid ammonia in a sealed tube.
The isoindoline derivative was isolated by evaporation of the solvent, and it was characterised as its picrate. Dichloro-silicon-tetrakis(4-n-pentyl)-phthalocyanine was prepared by the reaction of 5-n-pentyl-1,3-diminoisoindoline with silicon tetrachloride, in quinoline. The pigment was isolated by extraction into methylene dichloride. The organic layer was washed with dilute hydrochloric acid, but the compound could not be further purified as insufficient material was available. Instead, the somewhat impure dichloro-compound was allowed to react with methanol in hot xylene and the bis(methoxy)derivative was purified. The reaction time which was needed was very short compared with that of unsubstituted dichloro-silicon-phthalocyanine\(^{20}\). The reason for this was presumably the much increased solubility of dichloro-tetrakis(4-n-pentyl)-silicon-phthalocyanine in the reaction medium. Bis(methoxy)-silicon-tetrakis(4-n-pentyl)-phthalocyanine was purified by chromatography on deactivated alumina and its P.M.R. spectrum was obtained in deuteriochloroform.
No other di-alkoxy-silicon-tetrakis(4-n-pentyl)-phthalocyanines were prepared because insufficient starting material was available.

5-t-Butyl-1,3-diminoisoindoline was prepared from 4-t-butyl phthalonitrile by allowing it to react with liquid ammonia in a sealed tube at 110°. The product was found to crystallise from the reaction mixture as a colourless solid, in high yield.

Dichloro-silicon-tetrakis(4-t-butyl)-phthalocyanine was prepared by the reaction of 5-t-butyl-1,3-diminoisoindoline with silicon tetrachloride in quinoline, at reflux. Purification of dichloro-silicon-tetrakis(4-t-butyl)-phthalocyanine was found to be extremely difficult because of the polar nature of the compound, and so the slightly impure material was used in the preparation of alkoxy derivatives.

It was found that dichloro-silicon-tetrakis(4-t-butyl)-phthalocyanine would react with methanol at room temperature in about 15 minutes, to form bis(methoxy)-silicon-tetrakis(4-t-butyl)-phthalocyanine. This increased reactivity appeared to be fairly general and a number of di-alkoxy-silicon-tetrakis(4-t-butyl)-phthalocyanines were prepared.
Dichloro-silicon-tetrakis(4-t-butyl)-phthalocyanine was allowed to react with methanol, phenol, p-nitrophenol and p-methoxy-phenol. In each case the product was obtained analytically pure by column chromatography on deactivated alumina and the P.M.R. spectrum was measured. An unexpected finding was that bis(ethoxy)-silicon-tetrakis(4-t-butyl)-phthalocyanine proved extremely difficult to prepare, but this is in agreement with work by Kenney on unsubstituted bis(ethoxy)-silicon-phthalocyanine\(^{(20)}\). The compound appeared to be formed only slowly but it hydrolysed very rapidly upon exposure to atmospheric moisture, or on attempted purification by chromatography and so it was not possible to prepare an analytical sample.

None of the compounds which have been described so far in this section have a melting point below 350\(^{\circ}\). In an attempt to prepare a phthalocyanine complex having a very low melting point, dichloro-silicon-tetrakis(4-t-butyl)-phthalocyanine was allowed to react with oleyl alcohol.

Unsubstituted bis(octadec-9(cis)-en-1-oxy)-silicon-phthalocyanine was found to melt at 125\(^{\circ}\) (Section I). By substituting t-butyl groups around the periphery of the macrocycle in this compound, a
derivative has been obtained which is liquid at ambient temperature. The liquid phthalocyanine was extremely viscous as may be expected from the nature of the molecule. The properties of this complex are remarkable considering that its molecular weight is 1298; and it appears to be the first liquid phthalocyanine to be reported.

The reason for the extraordinary properties of this compound undoubtedly lies in the bulk of the alkyl substituents. It appears that the alkyl groups completely surround the macrocycle, in effect the phthalocyanine nucleus is encapsulated with hydrocarbon.

Upon cooling in a dry ice/acetone bath, the material was seen to solidify to a glass-like solid, but this slowly melted again as its temperature approached room temperature. No specific melting point could be observed due to the difficulty in seeing exactly when the material became liquid. Curiously, the compound was found to hydrolyse very quickly when exposed to atmospheric moisture.

An interesting fact associated with bis(octadec-9(cis)-en-1-oxy)-silicon-tetrakis(4-t-buty1)-phthalocyanine was that it appeared to undergo "alcohol exchange" with methanol. When the liquid phthalocyanine was allowed to stand under methanol for 2 days at room temperature, it was observed to solidify. The solid material was shown by P.M.R. spectroscopy to be bis(methoxy)-silicon-tetrakis(4-t-butyl)-phthalocyanine. This type of exchange has been reported previously with di-alkoxy-silicon-phthalocyanines, but usually high temperatures
have been needed\(^{(20)}\). A simple exchange at room temperature has not been observed previously.

iii) **Conclusions:** The main feature of interest in the chemistry of the di-alkoxy-silicon-tetrakis(4-alkyl)-phthalocyanines was the very high reactivity of the compounds. They appeared to be considerably easier to prepare than the parent unsubstituted complexes and also appeared to be considerably more susceptible to hydrolysis. This feature is undoubtedly due to the increased solubility of both the starting material and the product.

B) **Proton Magnetic Resonance Studies**

i) **Introduction:** The main purpose behind the preparation of the di-alkoxy-silicon-tetrakis(4-alkyl)-phthalocyanines was the study of their P.M.R. spectra, which were likely to have points of interest.

   1) It was expected that the alkoxy chains attached to the central silicon atom in the di-alkoxy-silicon-tetrakis(4-alkyl)-phthalocyanines would prevent aggregation of the molecules in concentrated solution, so that the chemical shifts would be independent of concentration.

   ii) It was expected that the groups attached to the central metal in the 5th and 6th co-ordinate positions would be strongly shielded diamagnetically. These co-ordinate positions have been used, in work by Kenney\(^{(20)}\)(33), and also in this work, to attach solubilising groups to the macrocycle. Alkyl substituents around
the periphery of the ring provide an alternative method for the solubilisation of the macrocycle and so leave the central silicon atom available for the substitution of groups which are of greater interest for P.M.R. study.

ii) Bis(phenoxy)-silicon-tetrakis(4-t-butyl)-phthalocyanine:

Di-alkoxy-silicon-phthalocyanines have been reported in the literature whose P.M.R. spectra would be interesting if only the compounds were sufficiently soluble. An example of a derivative of this type is bis(phenoxy)-silicon-phthalocyanine, which was reported by Kenney and coworkers in 1960\(^{(24)(82)}\).

![Structure of Bis(phenoxy)-silicon-tetrakis(4-t-butyl)-phthalocyanine]

This compound has been solubilised by the substitution of t-butyl groups around the periphery of the macrocycle. The protons associated with the phenoxy groups would be expected to experience a deshielding effect from their own phenyl ring, and hence a downfield shift. However the whole of the phenoxy groups are in the strongly shielding region of the phthalocyanine macrocycle and so would be expected to experience a large upfield shift. The precise magnitude of the latter effect was not known.
Fig XIV

OBSERVED SPECTRUM OF
BIS(PHENOXY)-SILICON-TETRAKIS(4-t-BUTYL)-PHTHALOCYANINE
The P.M.R. spectrum of bis(phenoxy)-silicon-tetrakis(4-t-butyl)-phthalocyanine is shown in Fig. XIV. An interesting feature of the spectrum was that the aromatic protons associated with the phthalocyanine macrocycle, appeared to be resolved. This is presumably due to the presence of the alkoxy substituents which prevent aggregation, as suggested earlier. Also the t-butyl signal, even in concentrated solution, was not split, as it was in the case of the metal free and nickel compounds. This is further support for the theory that the abnormal splitting of the corresponding signal observed in the P.M.R. spectra of the metal free and nickel complexes was due to molecular aggregation, and not to positional isomerism. However, the simplicity of the spectrum does not by itself eliminate the possibility of an isomer mixture being present. Indeed, as with the tetrakis(4-alkyl)-metal free and nickel derivatives, none of the di-alkoxy-silicon-tetrakis(4-alkyl)-phthalocyanines could be obtained in a crystalline state, which strongly suggested that each of these compounds is a mixture of peripheral positional isomers.

The phenoxy group, held immediately above the centre of the aromatic macrocycle, as expected, proved to be of interest. The protons associated with this phenyl ring appeared as two sharp multiplets centred at 4.35\(\tau\) and 7.52\(\tau\), corresponding to 3 and 2 protons respectively. The band envelope of these peaks showed a similarity in reverse to that from the ring protons of acetophenone, where the \(\alpha\)-protons resonate at lower field from the \(\beta\) and \(\gamma\) protons\(^{(83)}\).
Fig XV

OBSERVED SPECTRUM (a)

CHCl₃

T.M.S.

OBSERVED SPECTRUM (b)

CHCl₃

T.M.S.
Bis(p-nitrophenoxyl) and bis(p-methoxyphenoxyl)-silicon-tetrakis(4-t-butyl)-phthalocyanines were prepared by the reaction of dichloro-silicon-tetrakis(4-t-butyl)-phthalocyanine with p-nitrophenol and p-methoxyphenol respectively. The P.M.R. spectra of these compounds are shown in Fig. XV. The $\Delta^1\Pi\Pi^1$ system associated with the $p$-substituted phenoxy group was not fully resolved, the lines appearing as two doublets. In the case of bis(p-nitrophenoxyl)-silicon-tetrakis(4-t-butyl)-phthalocyanine, the doublets were centred at 3.45 and 7.5 and in the p-methoxyphenoxy analogue they were centred at 4.38 and 7.62. The p-methoxy protons appeared as a singlet at 7.0 and hence even these suffered considerable shielding by the macrocycle.

The main purpose in the preparation of these compounds was to study the effects of electron withdrawing and electron donating groups in the para-position of the phenyl ring upon the rate of hydrolysis of these compounds. If the mechanism of hydrolysis involved nucleophilic attack on the silicon atom, (Fig. XVI(a)) then the hydrolysis rate would be expected to be greater in the case of a p-nitro substituent.

The mechanism suggested by Kenney$^{(20)}$ is illustrated in Fig. XVI(b), and involves an intermediate siliconium ion. In this case, the substitution of a p-nitro group would be expected to decrease the rate of hydrolysis but a p-methoxy group would increase the hydrolysis rate.
Fig XVI

(a) [Diagram showing chemical structures with reaction arrows]

(b) [Diagram showing chemical structures with reaction arrows]
It was shown, in practice, that the hydrolysis of the \( p \)-methoxy-phenoxyp derivative was very much faster than the \( p \)-nitrophenoxy compound. Hence this is further evidence for the mechanism suggested by Kenney.

iii) **Bis(octadec-9(cis)-en-1-oxy)-silicon-tetrakis(4-t-butyl)-phthalocyanine**: The P.M.R. spectrum of bis(octadec-9(cis)-en-1-oxy)-silicon-tetrakis(4-t-butyl)-phthalocyanine was obtained in deuterio-chloroform, in order to compare the high field signals with those of the parent compound, without peripheral substitution. The chemical shift of the \( \alpha \)-methyleno group in the alkoxy chain was found to be 12.03 \( \tau \) which was identical with that of the analogue without t-butyl groups, reported in Section I. The lines associated with the alkoxy chain were broadened, indicating restricted movement of the chain. It would appear that the substitution of alkyl groups around the periphery of the ring had little effect upon the size of the induced ring current. The ring protons of the macrocycle again appeared resolved and the chemical shifts were similar to those of the phenoxy analogue.

iv) **Bis(methoxy)-silicon-tetrakis(4-t-butyl)-phthalocyanine**: This compound was prepared as described earlier and its P.M.R. spectrum indicated that molecular aggregation was again inhibited even though the alkoxy group was small. Experiments with the compound showed that none of the chemical shifts were concentration dependant (Fig. XII). The aromatic protons of the macrocycle were resolved and
appeared to resonate at similar field to other di-alkoxy-silicon-tetrakis(4-t-butyl)-phthalocyanines (Fig. XVIII). Hence it is suggested that the nature of the central metal alkoxy substituent has little effect upon the size of the induced ring current and therefore upon the aromaticity of the silicon phthalocyanine. The methoxyl signal appeared as a sharp singlet at 11.75 \( \tau \) as a result of the diamagnetic shielding by the macrocycle. The sharpness of the signal indicated completely free rotation of all bonds associated with the methoxy group and so the chemical shift was a true average value.

Comparison of the chemical shift of the methoxyl signal with that of the \( \alpha \)-methylene group along the alkyl chain in the case of long chain alkoxy compounds showed that the methyl appeared to lower field than the methylene signal. This is added confirmation for the hypothesis suggested in Section I, that completely free movement was not possible in the alkyl chain of di-alkoxy-silicon-phthalocyanines. The methylene protons in Fig. XVII(b) sweep out a more restricted volume of space, closer to the macrocyclic ring than do the methyl protons in Fig. XVII(a).

Hence the average chemical shift of the protons associated with the \( \alpha \)-methylene group would be to higher field than the methyl signal.

v) Bis(methoxy)-silicon-tetrakis(4-n-pentyl)-phthalocyanine: The preparation of this compound has been described earlier. The P.M.R.
Fig XVII

(a)

(b)
spectrum in deuteriochloroform was obtained and showed all the expected features. The high field methoxy protons came to resonance at 11.75\( \tau \), which was an identical shift to that observed in the case of the t-butyl substituted macrocycle. This confirmed the supposition that the nature of the alkyl substituent had little effect on the diamagnetic shielding of the macrocycle.

The aromatic protons of the macrocycle were again highly resolved but the band envelopes were of different shape from those of the analogous t-butyl substituted phthalocyanines.

The aromatic regions of the spectra of bis(methoxy)-silicon-tetrakis(4-t-butyl)-phthalocyanine and bis(methoxy)-silicon-tetrakis(4-n-pentyl)-phthalocyanine have been interpreted on a first order basis and are shown in Figs. XVIII and XIX. The para coupling, which would in any case be very small, was taken to be zero, in order to simplify the calculation. Insufficient resolution could be obtained at 60 Mc/s for a complete interpretation. A spectrum at 100 Mc/s is at present being obtained, but at the time of writing was not available for study. The chemical shifts and coupling constants are shown in Table IX.

It can be seen that \( \delta_A \) and \( \delta_X \) in the case of the t-butyl substituted macrocycle are 0.26 and 0.31 p.p.m. to lower field than in the case of either the n-pentyl substituted compound, or in the methyl substituted macrocycle, as reported by Sammes (32). This was not expected in terms of the relative inductive effects of t-butyl and
n-pentyl. Instead, an upfield shift would be expected. This deshielding effect of a t-butyl group attached to a phenyl ring upon the o-protons of the ring has been reported previously(64)(85). It has been attributed to intramolecular van der Waals forces between the bulky t-butyl group and the adjacent o-protons.

\[
\begin{array}{|c|c|c|}
\hline
 & \text{H}_A & \text{H}_A \\
\hline
\text{J}_{A1} & 0.56 \tau & 0.30 \tau \\
\text{J}_A & 0.46 \tau & 0.43 \tau \\
\text{J}_X & 1.86 \tau & 1.55 \tau \\
\varepsilon_{AX} & 1.40 \text{ p.p.m.} & 1.12 \text{ p.p.m.} \\
\text{J}_{A1X} & 1.7 \text{ c/s} & 1.8 \text{ c/s} \\
\text{J}_{AX} & 7.8 \text{ c/s} & 8.0 \text{ c/s} \\
\hline
\end{array}
\]

**TABLE IX**

C) **Experimental**

5-n-Pentyl-1,3-diiminoisoindoline

4-n-Pentyl phthalonitrile (1.0g) was heated in a sealed tube with liquid ammonia (3ml) and methanol (7.5ml) at 110° for 4 hours. The solution was then removed and was concentrated under reduced
-145-

pressure. Most of the solvent was removed and a pale yellow solid was seen to separate, and was filtered from the solution. It was washed with a little methanol and was dried. 5-n-Pentyl-1,3-diiminoisoindoline was collected as a yellow solid. Yield 680mg (62.5%).

5-n-Pentyl-1,3-diiminoisoindoline was characterised as its picrate by adding a solution of picric acid in ethanol to a solution of the imidine in ethanol. The picrate separated immediately as a yellow solid which was recrystallised from dioxan/water, m.p. 270°

C_{25}H_{23}N_{9}O_{14} requires C = 44.58 H = 3.44 N = 18.72%

Found C = 44.30 H = 4.70% N = 18.66%

Bis(methoxy)-silicon-tetrakis(4-n-pentyl)-phthalocyanine

a) Dichloro-silicon-tetrakis(4-n-pentyl)-phthalocyanine

5-n-pentyl-1,3-diiminoisoindoline (300mg), silicon tetrachloride (0.4 ml) and quinoline (5ml) were heated slowly to reflux during 30 minutes and heated at reflux for a further 30 minutes. Upon cooling, the reaction mixture was diluted with methylene dichloride, and the mixture was filtered to remove insoluble material. The filtrate was washed with dilute hydrochloric acid (3 x 100ml) and then twice with water. The solution was dried over magnesium sulphate and evaporated to dryness giving crude dichloro-silicon-tetrakis(4-n-pentyl)-phthalocyanine.
b) Bis(methoxy)-silicon-tetrakis(4-n-pentyl)-phthalocyanine

Dichloro-silicon-tetrakis(4-n-pentyl)-phthalocyanine, prepared above, was dissolved in a mixture of xylene (10ml) and methanol (5ml), and the mixture was refluxed, with stirring for 3 hours. The solution was filtered and the solid was washed with benzene. The filtrate and washings were evaporated to dryness by rotary evaporation and the residue was dissolved in dry benzene. The solution was chromatographed on deactivated alumina (Brockmann activity: 2) using benzene as eluent. The fast moving blue-green band was collected and evaporated to dryness. The solid was worked up with methanol.

Yield 32mg (10.4%).

\[
\text{C}_{54}\text{H}_{62}\text{SiO}_2 \text{ requires } C = 73.43 \quad H = 7.08 \quad N = 12.69%
\]

\[
\text{Found } C = 73.29 \quad H = 7.16 \quad N = 12.71%
\]

5-t-Butyl-1,3-diiminoisoindoline

4-t-Butyl phthalonitrile (5g) was dissolved in methanol (35ml) in a Carius tube, and liquid ammonia (12.5ml) was added. The tube was sealed and was heated at 110° for 4 hours. Upon cooling, the tube was opened, and 5-t-butyl-1,3-diiminoisoindoline was collected as a colourless crystalline solid by filtration of the reaction mixture.

Yield 3.4g (62%).

The product was characterised as its picrate by adding a solution of picric acid in ethanol to an ethanolic solution of the imidene. The picrate was precipitated immediately and was recrystal-
lised from 50% aqueous dioxan, m.p. 270° (decomp.).

\[ C_{18} H_{18} N_7 \text{ requires } C = 50.23 \quad H = 4.22 \quad N = 19.53\%
\]

\text{Found } \quad C = 50.32 \quad H = 4.16 \quad N = 19.36\%\]

\text{Dichloro-silicon-tetrakis(4-t-butyl)-phthalocyanine}

5-t-Butyl-1,3-diiminoisoindoline (300mg), silicon tetrachloride (0.4ml) and quinoline (5ml) were heated slowly to reflux during 30 minutes and refluxed for 30 minutes. Upon cooling the mass was dissolved in methylene dichlorido and washed with dilute hydrochloric acid (3 x 100ml) and then with water. The organic solution was filtered and dried over anhydrous sodium sulphate. It was evaporated carefully to dryness and dichloro-silicon-tetrakis(4-t-butyl)-phthalocyanine was collected. Yield 187mg (66%).

\text{Bis(phenoxo)-silicon-tetrakis(4-t-butyl)-phthalocyanine}

Dichloro-silicon-tetrakis(4-t-butyl)-phthalocyanine (180mg) was heated with phenol (500mg) in refluxing xylene (10ml), for 3 hours. The reaction was followed by T.L.C. The solvent was removed by rotary evaporation and the solid was dissolved in benzene. The benzene solution was chromatographed on alumina and the fast moving blue-green was collected. Evaporation of the solvent followed by work up with methanol yielded bis(phenoxo)-silicon-tetrakis(4-t-butyl)-phthalocyanine.

\[ C_{54} H_{53} N_8 Si_2 \text{ requires } C = 74.20 \quad H = 6.11 \quad N = 12.82 \quad Si = 3.21\%
\]

\text{Found } \quad C = 74.56 \quad H = 6.16 \quad N = 10.86 \quad Si = 3.12\%\]

10.96
**Bis(p-nitrophenoxy)-silicon-tetrakis(4-t-butyl)-phthalocyanine**

The procedure used in the preparation of this compound was identical with that of bis(phenoxy)-silicon-tetrakis(4-t-butyl)-phthalocyanine except that p-nitrophenol was used in place of phenol. Chromatography of the product and evaporation of the solvent yielded bis(p-nitrophenoxy)-silicon-tetrakis(4-t-butyl)-phthalocyanine.

\[ C_{60}H_{56}N_{10}O_{6}Si \] requires \[ C = 69.21 \ H = 5.42 \ N = 13.45 \ Si = 2.70\%
\]

Found \[ C = 69.75 \ H = 5.89 \ N = 12.36 \ Si = 3.20\%

**Bis(p-methoxyphenoxy)-silicon-tetrakis(4-t-butyl)-phthalocyanine**

5-t-Butyl-1,3-diiminoisoindoline (800mg) was heated with silicon tetrachloride (1ml) and quinoline (10ml) at reflux for 30 minutes. The procedure which was used was identical with that described above. The dichloro compound was allowed to react with p-methoxyphenol. The pigment was isolated after chromatography. Yield 185mg (19\%).

\[ C_{62}H_{62}N_{8}SiO_{4} \] requires \[ C = 73.63 \ H = 6.18 \ N = 11.08 \ Si = 2.78\%
\]

Found \[ C = 74.55 \ H = 6.37 \ N = 10.09 \ Si = 2.98\%

**Bis(octadec-9(cis)en-1-oxy)-silicon-tetrakis(4-t-butyl)-phthalocyanine**

Dichloro-silicon-tetrakis(4-t-butyl)-phthalocyanine was allowed to react with cloyl alcohol under the usual conditions. The eluate, after chromatography, was evaporated to dryness and finally heated on a steam bath under high vacuum to remove last traces of solvent. The
blue oil which remained was analysed.

\[
\text{C}_{34} \text{H}_{118} \text{N}_{8} \text{SiO}_{2} \text{ requires } C = 77.61 \text{ H} = 9.15 \text{ N} = 8.69 \text{ Si} = 2.16\% \\
\text{Found } C = 78.51 \text{ H} = 9.25 \text{ N} = 8.39 \text{ Si} = 2.43\%
\]

**Bis(methoxy)-silicon-tetrakis(4-t-butyl)-phthalocyanine**

Dichloro-silicon-tetrakis(4-t-butyl)-phthalocyanine (480mg) was heated in xylene (20ml) with methanol (5ml) to 60° for 30 minutes. The product was worked up according to the usual procedure and was dried under vacuum. Yield 296mg (62.5%).

\[
\text{C}_{50} \text{H}_{54} \text{N}_{8} \text{SiO}_{2} \text{ requires } C = 72.60 \text{ H} = 6.58 \text{ N} = 13.55 \text{ Si} = 3.39\% \\
\text{Found } C = 72.99 \text{ H} = 6.66 \text{ N} = 11.23 \text{ Si} = 3.15\% \\
11.32\%
SECTION IV
A) **Di-alkyl-tin-phthalocyanines**

The attachment of alkoxy chains to the central metal of the silicon phthalocyanines has been shown to be a suitable method of solubilising these compounds. It has been found recently that this method could also be applied to the germanium analogues with equally successful results\(^{(34)}\). A reasonable extension of this work appeared to be in the application of this principle to other group IV elements, and in particular to tin.

All attempts to prepare the corresponding di-alkoxy tin compounds by the reaction of dichloro-tin-phthalocyanine with long chain aliphatic alcohols, using a wide variety of conditions failed. No reaction appeared to take place.

Complete decomposition of the macrocycle has been reported in the literature, using sodium alkoxides\(^{(17)}\) and this may be due to the formation of an unstable di-alkoxy-tin-phthalocyanine which immediately decomposed. Alkoxyl tin derivatives are in general relatively unstable compared with alkoxy-silicon compounds. However, alkyl tin compounds are found to have remarkable stability and can be distilled at high temperatures without decomposition.

An extension of this work was the attempted preparation of di-alkyl-tin-phthalocyanines. Earlier attempts by Linstead and coworkers in this field had failed, but in view of the work on
silicon derivatives\(^{(33)}\), it was thought useful to repeat this work. Di-butyl-tin-dichloride was allowed to react with 1,3-diiminoisoin-
doline, and also with phthalonitrile in an attempt to prepare bis(n-butyl)-tin-phthalecyanine. However, in both cases the product which was isolated was shown to be dichloro-tin-phthalo-
cyanine. This rather peculiar reaction presumably involves the elimination of the butyl groups in some form, but this has not been investigated further.

Assuming that the elimination of an alkyl group is possible in this reaction, the use of a tetra-alkyl-tin would be expected to lead to the formation of a di-alkyl-tin-phthalecyanine. Tetra-
heptyl-tin was prepared and was allowed to react with 1,3-diiminoisoin-
doline and also with phthalonitrile. In neither case could any metallated phthalecyanine be isolated and only a trace of metal free phthalecyanine was obtained.

The reason for the absence of reaction may be due to the spherical symmetry of the tetra-alkyl-tin compound. A more successful approach may be the use of trialkyl-tin-halides or a tetra-alkyl-tin compound having more than one type of alkyl substituent. No attempts along these lines were made but there appears to be no reason why di-alkyl-tin-phthalocyanines should not be reasonably stable.

B) Bis(phthalecyanine)-tin

i) Introduction: Nothing has been described so far as to use of P.M.R.
-153-
spectroscopy to elucidate ambiguous structural features in phthalocyanine compounds.

An example of a phthalocyanine whose structure has never been fully elucidated is that which was prepared by Linstead and coworkers in 1936\(^{(17)}\), by the reaction of dichloro-tin-phthalocyanine with disodium phthalocyanine. The product was named stannic phthalocyanine but no experimental proof of structure was given apart from analytical results which indicated two phthalocyanine residues per tin atom. The compound was considerably more soluble in benzene than most other phthalocyanines which had been prepared, and when reprepared in 1961\(^{(86)}\) was isolated by column chromatography of a benzene solution. The visible spectrum was atypical, a notable feature being an unusually low energy band at 774\,nm, not observed in other phthalocyanines, and this indicated that it was not a 'normal' phthalocyanine complex. Elvidge showed by titration with potassium dichromate that the compound was in fact a complex of tin in its oxidation state IV\(^{(87)}\). Hence the metal had not undergone any reduction to the stannous state during the preparation of the 2:1 complex. It was shown by Sammes\(^{(88)}\) that the 2:1 complex was light sensitive and underwent slow photodecomposition to a metal free derivative and a tin IV complex, which was not characterised. Kenney and coworkers in 1964\(^{(89)}\), showed that thermal decomposition of bis(phthalocyanine)-tin lead to a mixture of metal free phthalocyanine and stannous phthalocyanine. Attempts to prepare samples of the
compound for single crystal X-ray studies had failed because of the
difficulty in crystallising the material. The complex crystallised
as small needles and it was found very difficult to obtain crystals of
suitable size for X-ray work.

It has been suggested that the compound may be an 8-co-ordinate
complex of tin⁹(0), but little evidence has been put forward for
this theory. However the similarity of the I.R. spectrum of this
complex with other phthalocyanines has been suggested as evidence for
the planarity of the rings.

The evidence available hardly supports any one of the possible
structures for the complex to the rigid exclusion of the others.
The only feature which appeared to stand out was the peculiarity in
the visible absorption spectrum which suggested that the aromatic
ring was in a unique environment. Suggestions as to the structure
of the complex have been based upon the equivalence of the two
phthalocyanine units but this had not been proved, to date. It may
be in fact that the tin atom is centrally situated in one phthalocya-

A further possibility was that the tin atom, in oxidation state
IV was tetrahedral and was centrally spaced between the two rings.
The tin atom may be covalently bound to the inner ring nitrogen atoms, 2 above the metal and 2 below the metal.

This structure would inevitably involve some buckling of the phthalocyanine macrocycle and this would have accounted for the anomalous visible absorption spectrum. However tetrahedral tin IV is a notably unstable state and tends towards an octahedral configuration whenever this is possible. Hence it seemed unlikely that a stable octahedral complex such as dichloro-tin-phthalocyanine should be converted into an unstable tetrahedral configuration with buckling of the phthalocyanine ring and consequent loss of aromaticity.

ii) Discussion: In order to solubilise bis(phthalocyanine)-tin, t-butyl groups were substituted around the periphery of one of the rings. Dichloro-tin-phthalocyanine was prepared by the method suggested by Linsestad(17). It was isolated and was purified by extractional crystallisation. A better method for the preparation of this compound however made use of 1-chloronaphthalene as a high boiling solvent and reaction was carried out at reflux(89). Tetrakis (4-t-butyl)-phthalocyanine—disodium was prepared from 4-t-butyl phthalonitrile and sodium pentoxide in 1-pentanol. Dichloro-tin-phthalocyanine was then allowed to react with tetrakis(4-t-butyl)-phthalocyanine—disodium in 1-chloronaphthalene. The apparatus was blackened with a lacquer in order to exclude light since it was suspected that the product was photosensitive.
The solvent was removed by distillation under reduced pressure and the product was dissolved in benzene. The mixture was chromatographed on deactivated alumina and two bands were observed. The first band which was blue-green in colour was shown to be tetrakis (4-t-butyl)-phthalocyanine which was presumed to arise from demetal-lation of the disodium derivative. The second band, which was blue, was found to have an identical visible spectrum to that found by Whalley for the known 2:1 complex. The eluate was evaporated to dryness and the solid was worked up with methanol. Tetrakis (4-t-butyl)-bis(phthalocyanine)-tin was isolated and was shown to have a high solubility in benzene and chloroform.

The P.M.R. spectrum of the compound was obtained in deuterio-chloroform. The aromatic region of the spectrum was very diffuse and was only observable as a very broad band from 0 - 2\(\tau\). However the t-butyl signal appeared as a singlet at 8.03\(\tau\). These results appeared to eliminate any suggestion of ring buckling since even very slight deviations from planarity would result in splitting of the t-butyl signal in the P.M.R. spectrum of the compound. The chemical shift of the t-butyl signal at 8.03\(\tau\) was at lower field than any
Signal from the t-butyl substituents in any of the phthalocyanines so far discussed in Sections II and III. Hence it was concluded that both rings of the compound were planar and aromatic and that there was no substance in the suggestion that the complex was one of tetrahedral tin in which the two rings were buckled.

However, it has still not been proved that the two phthalocyanine units were symmetrically situated with respect to the tin atom. In order to provide some evidence for this, tetrakis(4-t-butyl)-bis(phthalocyanine)-tin was prepared by an alternative method to that described above. Dichloro-tin-tetrakis(4-t-butyl)-phthalocyanine was prepared by allowing 4-t-butyl phthalonitrile to react with anhydrous stannous chloride at 250°C. The yield by this method was very low and a better method was found. 5-t-Butyl-1,3-diiminoisoindoline was heated with anhydrous stannous chloride in refluxing 1-chloronaphthalene. The chloronaphthalene solvent was removed and the product was extractively crystallised from benzene. Purification by chromatography was not very efficient, presumably due to the polar nature of dichloro-tin-tetrakis(4-t-butyl)-phthalocyanine. Unfortunately the compound could not be obtained analytically pure.

Sodium phthalocyanine was prepared by standard methods(17) and was allowed to react with dichloro-tin-tetrakis(4-t-butyl)-phthalocyanine in refluxing 1-chloronaphthalene. Light was again excluded from the reaction. The reaction mixture was worked up as in the first preparation of tetrakis(4-t-butyl)-bis(phthalocyanine)-tin.
Thus in reaction scheme I, the t-butyl substituted ring originated from the sodium phthalocyanine reactant whilst in scheme II it originated from the dichloro-tin reactant. If the two rings of the bis(phthalocyanine)-tin complex were not in equivalent positions with respect to the tin; i.e. if the tin atom was not centrally situated between the rings, then two different compounds would result by these methods of preparation. However only a single product was obtained.

The P.M.R. spectrum of the complex produced by reaction scheme II was identical with that from scheme I. The infra-red spectra of the two compounds are shown in Figs. XX and XXI. Fig. XX represents the spectrum of the complex produced by scheme I, and Fig. XXI represents the complex produced by scheme II. The spectra were identical indicating that the same compound was produced by both reactions. Hence it was concluded that the tin atom is symmetrically situated between the two phthalocyanine rings.

Other workers have noticed that metal-free phthalocyanine was produced as an impurity in the preparation of bis(phthalocyanine)-tin. This was assumed to arise from demetallation of sodium phthalocyanine
due to traces of water in the solvent. t-Butyl substituted metal free phthalocyanine was also noticed in our present studies using reaction scheme I.

However considerable quantities of t-butyl substituted metal free phthalocyanine were recovered from scheme II and this could not arise from demetallation of the sodium derivative since unsubstituted sodium phthalocyanine was used. The dichloro-tin-tetrakis(4-t-butyl)-phthalocyanine used in the reaction did not contain any metal free impurity and it is unlikely that it would suffer direct demetallation during the reaction. Since precautions to exclude light had been taken throughout it is unlikely that photodegradation of the product had taken place. This observation is rather curious since it cannot be explained by any of the evidence which is available on the complex, and there is obviously a need for more work in this field.

iii) Conclusions: It can be concluded from the above reasoning that the two phthalocyanine rings in the bis(phthalocyanine)-tin complex are equivalent with the tin atom existing mid-way between them. The theory suggesting ring buckling has been disproved and it is concluded that the rings remain in a planar configuration.

It is suggested that bis(phthalocyanine)-tin may be a true 'sandwich' compound having a structure similar to the ferrocene complexes. Ferrocene systems have only been observed previously with the cyclopentadienyl anion, benzene, and the tropylium cation. An aromatic ring with the dimensions of phthalocyanine poses great
problems when considering the nature of the bonding involved. This is made more difficult by the fact that bonding in the ferrocene complexes is still not fully understood.

Several unsuccessful attempts have been made by earlier workers to prepare a sample of unsubstituted bis(phthalocyanine)-tin which was suitable for X-ray studies. Suitable crystals have now been prepared but no results were available at the time of writing. However they should eventually prove the structure of the sandwich complex unambiguously.

C) Experimental:

Bis(n-butyl)-tin-phthalocyanine

i) Dibutyl-tin-dichloride (2g) was dissolved in 1-chloronaphthalene (40ml) and phthalonitrile (3.3g) was added. The mixture was heated slowly to reflux on a metal bath and was refluxed for a further 3 hours. A reaction appeared to take place at 240° and the mixture slowly turned green. Upon cooling, the reaction mixture was filtered and a crystalline solid was obtained. The substance was shown to be dichloro-tin-phthalocyanine. Yield 384mg (8.6%).

ii) Dibutyl-tin-dichloride (2g) and 1,3-diminoisoindoline (3.8g) were heated slowly in 1-chloronaphthalene. The reaction mixture became brown at 160° and ammonia was evolved. The mixture was refluxed for 30 minutes when the solution became green and a solid
was deposited, which was shown to be dichloro-tin-phthalocyanine.

Yield 550mg (12%).

Tetrahexyl-Tin (91)

Magnesium turnings (2g) were added to dry ether (10ml) in a 250ml flask. A mixture of hexyl bromide (13.5g) in dry ether (10ml) was then added dropwise, and the mixture was heated on a water bath until reaction set in. The mixture was then refluxed gently for 30 minutes.

Anhydrous stannic chloride (3.5g) was added dropwise over 20 minutes and the reaction mixture was refluxed for a further hour.

The ether was removed by distillation over one hour. After cooling, a further portion of ether (25ml) was added and the mixture was cooled in ice water (3.5ml) and then 10% hydrochloric acid (17ml) was added dropwise to decompose the complex. The ethereal solution was separated and the aqueous layer was extracted with ether. After drying over anhydrous calcium chloride, the ether was removed and the residue was vacuum distilled giving tetrahexyl-tin b.p. 172-176°C/0.8mm; nD 1.4732; Lit. b.p. 209°C/10mm; nD 1.4706 (92).

Bis(n-hexyl)-tin-phthalocyanine

i) Tetrahexyl-tin (459mg) and phthalonitrile (512mg) were heated slowly to reflux in 1-chloronaphthalene. After 45 minutes no solid material was deposited, even after removal of the solvent.

ii) Tetrahexyl-tin (459mg) and 1,3-diiminoisoindoline (500mg) were
heated gently to reflux in 1-chloronaphthalene, during 15 minutes and refluxed for 30 minutes. After standing overnight 50mg of metal free phthalocyanine were deposited.

**Dichloro-tin-phthalocyanine**

i) Phthalonitrile (8g) and powdered anhydrous stannous chloride (2.5g) were heated together at 210° for 15 minutes. The product was cooled and exhaustively extracted with ethanol and then dried. It was extractively crystallised from o-dichlorobenzene. Yield 4g (58%).

ii) Phthalonitrile (10g) and anhydrous stannous chloride (4g) were refluxed in 1-chloronaphthalene (110ml) for 3 hours. The reaction mixture was cooled and the product filtered off. It was washed with benzene and ethanol and then continuously extracted with acetic acid and ethanol. Dichloro-tin-phthalocyanine was removed and dried. Yield 8.5g (62%).

**Tetrakis(4-t-butyl)-phthalocyanine-disodium**

Sodium metal (350mg) was allowed to react with dry 1-pentanol (10ml) and the mixture was heated to reflux. 4-t-Butyl phthalonitrile (4g) was added and the solution was refluxed for 10 minutes. It was cooled, filtered and the solid washed with a little dry propanol and then with benzene. The pigment was collected and dried under vacuum. Yield 1.07g (25%).
Tetrakis(4-t-butyl)-bis(phthalocyanine)-tin: (Scheme I)

Dichloro-tin-phthalocyanine (625mg) was heated in 1-chloronaphthalene (65ml) at reflux for 15 minutes. The apparatus was coated with camera black lacquer in order to exclude light. Tetrakis(4-t-butyl)-phthalocyanine-disodium was added and the mixture was refluxed for 90 minutes. The product was dissolved in benzene and the solution was filtered. The filtrate was chromatographed on deactivated alumina. The first blue band to be eluted was shown to be tetrakis(4-t-butyl)-phthalocyanine and the second blue band was found to be tetrakis(4-t-butyl)-bis(phthalocyanine)-tin. Yield 100mg (11.5%).

C_{50}H_{64}N_{16}Sn requires C = 70.23 H = 4.72 N = 16.38 Sn = 8.68%

Found C = 70.08 H = 4.91 N = 16.19 Sn = 8.18%

Disodium Phthalocyanine

Sodium metal (18.8g) was allowed to react with dry 1-pentanol (100ml) and heated to just below reflux. Phthalonitrile (20g) was added and the solution refluxed for 10 minutes and then filtered hot. The solid was extracted with dry benzene overnight and then dried. Yield 11g (51%).

Dichloro-tin-tetrakis(4-t-butyl)-phthalocyanine

1,3-Diminoisoindoline (1.2g) was heated with anhydrous stannous chloride (450mg) in 1-chloronaphthalene at reflux for 90 minutes.
Upon cooling, the solution was filtered and the solid was extractively crystallised from benzene. Filtration gave dichloro-tin-tetrakis (4-t-butyl)-phthalocyanine. Yield 450mg (41%). Attempts to further purify the product by chromatography, failed.

Tetrakis(4-t-butyl)-bis(phthalocyanine)-tin; (Scheme II)

Dichloro-tin-tetrakis(4-t-butyl)-phthalocyanine (500mg) was heated to reflux in 1-chloronaphthalene (65ml) and freshly prepared disodium phthalocyanine (500mg) was added. Refluxing was continued for 90 minutes and the solvent was removed. The residue was dissolved in benzene and filtered. The filtrate was chromatographed on alumina and the second blue band was collected. The eluate was evaporated to dryness and the solid was worked up with methanol. Yield 85mg (11.5%).

\[
\text{C}_{80}\text{H}_{64}\text{N}_{16}\text{Sn} \quad \text{requires} \quad \begin{align*} 
C &= 70.23 \\
H &= 4.72 \\
N &= 16.38 \%
\end{align*} \\
\text{Found} \quad \begin{align*} 
C &= 70.31 \\
H &= 4.92 \\
N &= 16.31
\end{align*}
\]

Bis(phthalocyanine)-tin

Dichloro-tin-phthalocyanine (1g) was added to 1-chloronaphthalene (180ml) and the mixture was refluxed for 20 minutes. Disodium phthalocyanine (0.8g) was added and refluxing continued for 90 minutes. The solvent was removed and the residue dissolved in benzene and the benzene solution chromatographed on alumina. The blue band was collected and evaporated to dryness. The product was extractionally
crystallised from benzene.

In order to prepare a highly crystalline sample, a saturated solution in benzene, of the pure complex was prepared and was allowed to evaporate slowly at room temperature in the dark over a period of 3 months without disturbing the solution. The crystals were removed from the sides of the flask in dry ether, filtered with great care and dried.
SECTION V
AROMATICITY OF THE MACROCYCLE

A) Introduction

An aromatic compound has been described as, "a compound which will sustain an induced ring current" (93). Benzene is the model aromatic system and its symmetry shows there is complete delocalisation of the six $\pi$-electrons. Other monocyclic aromatic systems may have different degrees of delocalisation of their $\pi$-electron systems, and so may sustain different effective ring currents.

By measuring the induced ring current it is possible to gain some idea of the magnitude of the $\pi$-electron delocalisation. Proton chemical shifts provide the best way of measuring the induced ring current and hence give a measure of the degree of the $\pi$-electron delocalisation. By comparing the proton chemical shift of a suitable group attached to the aromatic ring with that of a similar group associated with benzene, after making allowances for molecular dimensions etc., a value for the aromaticity of the compound can be obtained, with respect to benzene as standard.

B) Calculation

In order to treat the phthalocyanine macrocycle, it is best considered as a tetrabenzo substituted 18 $\pi$-electron ring system. This is not strictly correct since there would be complete delocalisation over the whole system.
The chemical shift of a t-butyl group on the periphery of the phthalocyanine system was considered as made up from two contributions, one from its own phenyl ring and the other from the inner macrocycle. The effects of the other benzene rings on this one group were considered to be negligible as was indeed indicated by the Johnson-Bovey shielding diagram.

During this work, the t-butyl substituted metal free derivative was considered and the aromaticity which was determined relates to the inner macrocyclic ring. The combination of the values for the inner macrocycle and the outer benzene rings is difficult and was not considered here.

The choice of a suitable group substituent for study is limited for solubility reasons, but the t-butyl group was considered to be suitable for two reasons.

1) The distance of the "average proton" of this group from the centre of each aromatic ring could easily be obtained since it would lie in the plane of the macrocycle.

2) The t-butyl protons were sufficiently distant from the rings, and the heteroatoms that inductive effects could be neglected.

The point-dipole approximation indicates that the ring current shift (i.e. the shift of a proton which can be assigned exclusively to the induced ring current) is proportional to the area of the ring
and to the number of \( \pi \)-electrons. The shift at a particular point is also inversely proportional to the cube of the distance from the ring centre.

\[
\text{R.C.S.} \propto \text{Area of Ring} \times \text{No. } \pi \text{-electrons} \times \frac{1}{(\text{Dist. from centre of ring})^3}
\]

The approximation assumes that the rings are circular. The radius of the inner ring and that of the benzene ring were obtained from a scale drawing of the macrocycle (1 inch = 1\( \AA \)), the dimensions taken being those obtained from X-ray measurements\(^{(15)} \). The radius of the inner macrocycle was taken as the distance of the centre of the ring to a bridge nitrogen atom.

"Average" Proton: For the calculation, the distance of an 'average' \( t \)-butyl proton from the centre of the benzene ring and also the inner macrocycle were required. The following approximations were made to obtain those values.

The known dimensions of a \( t \)-butyl group were obtained\(^{(97)} \), and were superimposed on the scale diagram. Fig. XXII illustrates the method used to obtain the distance of the 'average proton' from the benzene ring centre. The C-H distance \( (x) \) was projected on to the C-C axis as shown and the point Z obtained. The distance MZ was taken as the distance of the average proton from the benzene ring centre.

This distance was not applicable when the inner macrocycle was
Fig XXII

Fig XXIII
considered. Fig. XXIII illustrates the way this new value was obtained. The distance MZ was projected on to the axis shown and the point Y was taken as the position of the average proton. PY gave the distance of the average proton from the centre of the macrocycle.

The observed values are shown in Table X

<table>
<thead>
<tr>
<th></th>
<th>Benzene Ring</th>
<th>Inner Macrocycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radius (r) (Å)</td>
<td>1.39</td>
<td>3.3</td>
</tr>
<tr>
<td>No. of π-electrons (N)</td>
<td>6</td>
<td>18</td>
</tr>
<tr>
<td>Dist. of 'average' proton from centre of ring (d)(Å)</td>
<td>4.17</td>
<td>9.25</td>
</tr>
</tbody>
</table>

**TABLE X**

The chemical shift of the t-butyl protons attached to phthalocyanine were obtained by extrapolation to infinite dilution of the values obtained at various concentrations of the metal-free pigment in deuteriochloroform. The chemical shift of a t-butyl group attached to benzene was also required and was obtained from an authentic sample of t-butyl benzene in deuteriochloroform as solvent. The chemical shift of a "free" t-butyl group was obtained as a reasonable approximation from the shift of the t-butyl signal of 2,2,4-trimethylpentane. Here inductive effects would be minimal. These values in deuteriochloroform compared well with literature values which were obtained in carbon tetrachloride. They are listed in Table XI.
### TABLE XI

From these observations the following values could be derived:

- **Ring Current Shift of t-butyl due to macrocycle** = $8.69 - 8.14 = 0.55$ p.p.m.

- **Ring Current Shift of t-butyl due to benzene** = $9.13 - 8.69 = 0.44$ p.p.m.

**Maximum possible ring current shift for macrocycle** (i.e. if aromaticity = 1)

\[
= R.C.S_{\text{benz}} \times \frac{(r_{\text{mac}})^2}{(r_{\text{benz}})^2} \times \frac{N_{\text{mac}}}{N_{\text{benz}}} \times \frac{(\delta_{\text{benz}})^3}{(\delta_{\text{mac}})^3}
\]

\[
= 0.44 \times \left(\frac{3.3}{1.39}\right)^2 \times \frac{18}{6} \times \left(\frac{4.17}{9.25}\right)^3
\]

\[
= 0.68
\]

- **Aromaticity of the macrocycle** = \(\frac{0.55}{0.68}\) = ca 81%
It must be noted however that this value is, at best, very approximate. The dimensions of the inner macrocyclic \( \pi \)-electron system are difficult to define. In the calculation they were assumed to occupy a circle whose radius corresponded to the distance of the macrocycle centre to a bridge nitrogen atom.

C) Aromaticity of Bis(phthalocyanine)-tin

If this compound had a 'sandwich' structure as was suggested in section IV then the bonding would presumably be due to overlap of the \( \pi \)-electron system with vacant metal orbitals which were suitably oriented. Hence the two free electrons associated with each macrocycle would probably be delocalised over the aromatic system.

The calculation which has been reported was carried out again using the new value for the number of delocalised electrons. The value for the aromaticity of the macrocycle (i.e. 81\( \mu \)) was used, and it was possible to calculate the expected chemical shift of the t-butyl protons of the sandwich compound.

It must be emphasised that many approximations have been made in these calculations but it is interesting to note that the calculated chemical shift for the sandwich compound was 8.07\( \tau \), a downfield shift of 0.07 p.p.m. This corresponds well with the observed chemical shift of 8.03\( \tau \), a downfield shift of 0.11 p.p.m.

When considering any other structure for bis(phthalocyanine)-tin,
a downfield shift in the t-butyl signal was very difficult to account for. Hence this approach seems to add further proof that the structure of bis(phthalocyanine)-tin is of a true sandwich complex.
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