EXPERIMENTS TOWARDS NEW MACROCYCLIC

COMPOUNDS FROM 1,3-DIIMINOISOINDOLINE

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SUMMARY

The work described in this thesis is concerned with the reaction of various five-membered heterocyclic diamines with diiminoisoindoline, leading to macrocyclic aza-linked compounds whose skeletal structure resembles phthalocyanine. However, the reaction of 2,5-diamino-3,4-dicyanothiophene and 1,3-diiminoisoindoline, in dimethylformamide, gave rise exclusively to an open chain compound, from the condensation of one unit of the first reagent with three units of the second. In 2-methoxyethanol the same reactants gave an intermediate two unit compound, 1-imino-3-(5-amino-3,4-dicyano-2-thienyl)iminoisoindoline, which could be converted into the unsymmetrical four-unit compound above, but the latter failed to cyclise under a variety of conditions.

In the course of the studies on the two-unit intermediate compound, an anomalous reaction was encountered with benzaldehyde, giving a reduced product rather than the simple Schiff's base. Similar anomalous reactions were found with diiminoisoindoline and oxoisoindoline, giving reduced products postulated as arising via a hydride transfer reaction.

Condensation of guanazole (3,5-diimino-1,2,4-tetrahydrotriazole) and diiminoisoindoline gave a macrocyclic compound in good yield, having a 2:2 structure. Analogous compounds were prepared from 1-phenylguanazole and from t-butyldiiminoisoindoline. Metal containing macrocycles were also obtained, using the above reactants and the bivalent transition metal acetates of Co, Ni, Cu, Zn and Hg, showing characteristics similar to those of previously reported cross-conjugated macrocycles. They were thermally stable and highly insoluble in organic
solvents.

Among the model compounds prepared, were two and three-unit products from oxoisoindoline or 1-imino-3-phenyliminoisoindoline and guanazole or 1-phenylguanazole these had the expected characteristics.

A series of condensations of the guanazoles with either benzaldehyde or anisaldehyde, gave a variety of Schiff's base products, either mono or dianils depending on the conditions used.

The reaction of 2,5-diamino-3,4-dicyanothiophene and oxoisoindoline in 2-methoxy- and 2-ethoxyethanol gave unexpectedly complex products incorporating the solvent in a condensed macromolecule. In anhydrous ammonia, under pressure, the thiophene gave only linear polymeric products and no macrocyclic materials.
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Historical Introduction

Studies on the Pinner reaction of phthalonitrile resulted in 1952 in the isolation and characterisation of 1,3-diiminoisoindoline (I). At this time an I.C.I. patent described a facile preparation of this imidine from the reaction of phthalonitrile and methanolic ammonia under pressure.

This new imidine was closely related to 1-imino-3-oxo isoindoline (II), which had been described somewhat earlier by A. Braun and J. Toherniac, prepared by the thermal isomerisation of ortho-cyanobenzamide at 200°. This compound had been the subject of further study, in which it was found that the exocyclic imino group was reactive, in particular it readily condensed with amines with the elimination of ammonia.

Both exocyclic groups of the new base were found to be similarly reactive towards amines, evolving ammonia and giving well defined products. For example with 2-aminopyridine, 1:3-di-2'-pyridyliminoisoindoline was obtained (III). This latter compound behaved as a tridentate ligand and formed metal complexes readily.

An extensive study of the light absorption properties of the imidine and many, "fixed bond", derivatives led to the conclusion that the base itself exists predominantly in the diimino form as written and not in the amino-imino form. In derivatives, the substituents clearly affected the proportions of the two tautomeric forms.

The discovery that both imino functions of this imidine could react with primary aromatic amines led to the construction of an entirely new type of macrocyclic compound. Thus when 2,6-diaminopyridine and 1,3-diiminoisoindoline underwent reaction, eliminating ammonia, they yielded a macrocyclic compound with the structure (V).
This new macrocycle showed considerable thermal stability, and the property of forming metal complexes of a type similar to those of phthalocyanine. The central sixteen-membered ring was similar in size and shape to that found in phthalocyanine, and the pyridine nitrogen atoms could perform a similar coordinating function to those of the second pair of isoindole nitrogens in phthalocyanine. Thus the macrocycle \((V)\) combined with bivalent, tetracoordinate metals capable of existing in a planar symmetry to form stable derivatives. An X-ray analysis of the nickel derivative confirmed the macrocyclic structure, and further showed that the isoindole and pyridine residues were alternately tilted out of this plane through 25°, in opposite directions to each other. Thus the molecule has a shallow saddle-like structure.

Subsequent work led to the discovery that this condensation reaction was by no means specific for 2:6-diaminopyridine and could be readily extended giving analogous macrocyclic compounds of the general type \((VI)\), where \(R\) was meta-phenylenediamine, 2,7-diaminonaphthalene, 2,8-diminoacridine and 3,5-diaminopyridine. More recently analogous macrocyclic species have been reported in which \(R\) is 2,7-diaminodiphenylene sulphone or 2,7-diaminofluorene.

In the above series of molecules only the 2,6-diaminopyridine macrocycle showed the formation of a metal complex in which the metal lay within the central ring. The 3,5-diaminopyridine macrocycle was found to form complexes with several metals but these were not thought to be of the above type. A subsequent claim has been made for the preparation of analogous metal derivatives of the benzene macrocycle, in which the divalent
ions Cu$^{2+}$, Co$^{2+}$, Ni$^{2+}$, Zn$^{2+}$, Cd$^{2+}$ were employed. \(^{11}\)

It was observed that the introduction of a metal into the central, "hole", of structure (V) produced a pronounced bathochromic shift in the light-absorption spectrum compared with the metal free macrocycle. The suggested explanation of this shift, not observed in the phthalocyanine series, was that whilst the parent structure (V) exists in a cross conjugated form, the metal derivatives might have a fully conjugated arrangement of double and single bonds round the large ring. Such a completely conjugated system would be expected to show higher wavelength absorption. The contribution of this latter structure might well vary with the metal chelated.

During the course of the work on the preparation of the above macrocycles a number of compounds were isolated and identified as having intermediate structures between the reactants and the final cyclic product.\(^{12}\) The isolation of these intermediate compounds indicated that the condensation of an imidine with an amine took place step-wise. Among the many intermediates of this type prepared, two (VII) and (VIII), serve to illustrate the details of the reaction leading to macrocycle formation, and to provide a route to a new macrocyclic species. Both of the compounds (VII) and (VIII) condense with meta-phenylenediamine to give the expected macrocycle. With 1,3-diiminoisoindoline, however, they give rise to a new type of macrocycle having three-quarters the structure of phthalocyanine (IX). This macrocycle contains only one replaceable hydrogen in the central ring and early attempts to prepare metal derivatives were not conclusive. R.P. Smirnov and E.D. Berezin, however, have more recently reported the preparation of metal complexes of this ligand, in which the
metallated macrocycle acts the part of a cation (X). These authors found that the macrocycle was cross conjugated in the metal free state as was reported previously, but gave rise to a new chromophore characterised by higher wavelength absorption on the introduction of a metal into the ring.

A more recent publication reports the formation of metal derivatives of the pyridine analogue of (IX). The technique employed in this case was to prepare metal complexes of the pyridine material having structure (VIII). Condensation with 1,3-diiminoisoindoline in a "template synthesis", gave the metal macrocycle. The presence of the metal atom appears to hold the molecule in the required sterochemical environment for easy condensation, since reaction without the presence of metal posed considerable difficulties.

A fully conjugated macrocycle was obtained from the reaction of succinimidine and diiminoisoindoline, in which the benzene ring of (IX) is replaced by a pyrrole ring. This new macrocycle closely resembled phthalocyanine and formed analogous metal complexes.

A series of recent publications has considerably extended the work outlined above. Thus V.P. Borodkin and his co-workers in Russia have reported macrocycles of the type (VI), in which one of the R groups is 4-chlorotriazine, and the other is either benzene, pyridine, pyrimidine or the triazole guanazole. Metal complexes of these "mixed" macrocycles are also reported.

A further series of macrocycles analogous to (VI) and (IX) have been prepared by F.P. Snegireva and V.N. Klyuev, also in Russia, in which two of the carbon atoms on the isoindole ring have been
replaced by sulphur. The synthesis of these latter macrocyclic materials stems from the preparation of 1,3-diiminothioisoindoline (XI) by these authors.

The macrocycles referred to above show a considerable formal resemblance to phthalocyanine and its derivatives, but they are not so extremely stable, thermally, nor do they absorb light at such long wavelengths. The unique phthalocyanines, discovered in 1928, were investigated in detail by R.P. Linstead and his colleagues in the early 1930's, resulting in the well known macrocyclic structure. Commercial interest in the properties and uses of phthalocyanine and its metal derivatives was quickly aroused and there has been an intensive study of these molecules, which seems still to be gathering momentum. Phthalocyanine is readily prepared from simple starting materials, it shows quite exceptionally high thermal and light stability and has good tinctorial characteristics.

Linstead's original series of papers described syntheses of phthalocyanines from phthalonitrile and a metal or metal salt. Similar analogous products were prepared, containing the basic phthalocyanine structure, from a number of aromatic ortho substituted dinitriles, though the stability of these latter materials was generally lower than that of phthalocyanine itself. The discovery of 1,3-diiminoisoindoline led to its reductive self condensation, giving phthalocyanine in higher yield than from phthalonitrile.

The large number of literature reports on phthalocyanine and its compounds has been reviewed recently. Phthalocyanine forms metal complexes with the majority of metals known. The divalent metal complexes are the most common, although complexes are known
having metals in all oxidation states from zero to six. An unusual complex with tin has been reported having a ferrocene 32, 33 sandwich-type structure.

Polymeric phthalocyanines are known, as well as polymeric derivatives of the benzene macrocycle of (V). These latter polymers are prepared from 1,2,4,5-tetracyanobenzene and meta-phenylenediamine. 34, 35

A common physical characteristic of the macrocyclic compounds referred to above and of the phthalocyanines, is that of low solubility in organic solvents. A number of more soluble phthalocyanines have been reported arising from the substitution 36 of the aromatic benzene rings, and from octahedral metal phthalocyanines. Thus bis (triethylsiloxy) germanium and dichloro-tin phthalocyanines have been prepared which are soluble in organic solvents.

The common explanation of the low solubility of these macrocycles is that the geometry of the ring system is such as to allow strong intermolecular interaction enabling the molecules to, "stack" regularly into the crystal lattice. The strong intermolecular interaction prevents solvent molecules permeating between the layers. X-ray analysis of a number of metal phthalocyanines and of the nickel complex of the pyridine macrocycle (V), show that there is likely to be considerable interaction between the central metal atom in one molecule and a corner nitrogen on adjacent rings above and below. Magnetic and electrical properties of the phthalocyanine series seem to confirm that considerable interaction occurs between adjacent parallel molecules. 31

A structural modification leading to soluble phthalocyanine
compounds was devised by L. Shuttleworth, who substituted the peripheral hydrogen atoms in a series of phthalocyanines by tert-butyl groups. The considerably increased solubility of these alkylated products has been explained as arising from steric hindrance to stacking and to an increased area of solvation. More recently this technique has been extended to the synthesis of the alkylated analogue of (V), though not without some difficulty. The condensation of 5-tert-butyl-1,3-diminoisindoline and 2,6-diaminopyridine went only in the presence of a metal salt.

The introduction of tert-butyl and other alkyl groups has been found to lower the melting points of the molecules compared with the non-alkylated compounds, a consequence of lowering the lattice energy of the solid.

The increased solubility of the alkylated phthalocyanines enabled proton magnetic resonance spectra of them to be obtained. The spectra found agreed well with previous determinations on dipotassium phthalocyanine dicyanoferrate (II) and dipotassium tetra-4-methylphthalocyanine dicyanoferrate (II). The effects arising from the induced ring current on the chemical shifts of the alkyl groups have been used to provide an estimate of the aromaticity of phthalocyanine compared to benzene, a value of 81% being found for tetra (4-t-butyl) phthalocyanine.

The preparation of macrocyclic compounds of the type illustrated by (V) and (IX) have until now, centered almost entirely upon the use of six-membered aromatic amines and fused six-membered ring systems. An exception is the preparation of tribenztetrazaporphyrin. It would be expected that similar products could
be obtained using five-membered heterocyclic aromatic diamines of the pyrrole, thiophene and furan series. Among the interesting points which would arise from the syntheses of these hypothetical macrocycles would be their complexing properties with metals. The lack of reports of this type of macrocycle would seem to reflect the unavailability of relatively stable five-membered heterocyclic diamines.

An interesting exception to the last statement is the triazole system (XII), first prepared, and named guanazole, by G. Pellizzari in 1894. Two tautomeric forms have been written, since to date no convincing demonstration of either form has been made. Pellizzari himself favoured the diimino form on the basis of chemical reactivity, while later workers favoured an amino-imino form, from the light absorption data of certain derivatives.

A patent published in 1960 reported the formation of red-brown powders when this compound or derivatives of it, were heated with diiminoisoindoline in dimethylformamide in the presence of oxalic acid, ammonium phosphate and metal chlorides (Ni $^{2+}$ and Cu $^{2+}$). No evidence, however, was given of the type of material obtained. Very recently V.P. Borodkin and his colleagues reported the preparation of a mixed, cross-conjugated macrocycle, containing a guanazole residue and a triazine residue, replacing the pyridine rings in structure (V).

Another stable aromatic diamine system was reported resulting from the preparation of the cyanocarbon compound tetracyanoethylene. This versatile compound was found to give, on reaction with hydrogen sulphide in the presence of basic catalysts, the compound 2,5-diamino-3,4-dicyanothiophene. This thiophene was found to be
unusually stable, presumably because of the presence of the strongly electron withdrawing nitrile groups, since aminothiophene itself is unstable and has only been isolated as the stannic chloride double salt.

An interesting reaction of this diaminothiophene has been reported by Von G. Manecke and D. Wohrle, in which the molecule undergoes self condensation. They report that reaction at 300° in the presence of cuprous chloride leads to a black insoluble material. On the basis of elemental composition and infra-red analysis the authors attribute a sheet-like polymeric structure to this material (XIII).

The basis of the work carried out in this thesis was the reaction of diiminoisoindoline with these five-membered heterocyclic diamines, with a view to preparing and investigating macrocyclic compounds of the types (V) and (IX).
Chapter 2.

(i) The reaction conditions under which 1,3-diiminisoindoline and 2,5-diamino-3,4-dicyanothiophene were reacted were initially determined by the solubility properties of the thiophene. The authors who first described this compound reported that it was soluble only in dimethylformamide. This solvent, however, was not without its advantages, both reactants dissolving in it, and it has a reasonably high boiling point with little decomposition when under an atmosphere of nitrogen.

In a preliminary experiment 1:1 stoichiometric proportions of reactants were dissolved in a small quantity of dry dimethylformamide, and a stream of nitrogen gas was allowed to play over the solution and flush air out of the reaction vessel. After ten minutes flushing, heating was commenced and the stirred mixture just brought to reflux conditions. The use of a stream of nitrogen served to provide an inert atmosphere and to remove any ammonia liberated from the reaction, so displacing any equilibria to the side of products. After twenty minutes heating, a bright yellow solid began separating. This then gradually redissolved on further heating for an hour or so. Much ammonia was evolved during this time. At the end of a four hour period, the ammonia evolution had virtually ceased. A very small amount of a brown powdery solid was collected which did not melt up to $350^\circ$ but tended to decompose at this temperature. An infra-red spectrum of this material showed very weak bands for N-H stretch and nitrile absorption together with aryl absorption. Work up of the filtrate gave no distinct products.
From this preliminary experiment it was clear that condensation was taking place, and it was not giving rise to any appreciable amount of phthalocyanine, as would occur if the imidine condensed with itself exclusively. Accordingly an attempt was made to isolate the initial yellow insoluble product.

Stoichiometric proportions of reactants were heated in a minimal volume of dimethylformamide for 15 minutes and the solid which separated was filtered off, washed with fresh solvent and dried, to give a powdery yellow solid, showing no definite melting point but decomposing above 337° and turning red. A further small quantity of the same material separated from the filtrate on standing at room temperature for several days.

The sodium fusion test demonstrated the presence of sulphur and nitrogen in the product. The material was generally insoluble in organic solvents, dissolving sparingly in 1-chloronaphthalene, ortho-dichlorobenzene and dimethyl sulphoxide. A mass spectrum indicated a molecular ion of m/e 549+, that of the expected 2:2 macrocycle being 550.

Attempted high vacuum sublimation gave rise to decomposition and an unattractive strongly coloured sublimate, and an even darker residue. Attempts made to crystallise the product from the above mentioned solvents usually resulted in the formation of a glassy gel, which on drying under high vacuum gave a powdery solid. After several, "recrystallisations", from ortho-dichlorobenzene, and thorough washing and drying, an elemental microanalysis corresponded to a formula of C_{30}H_{15}N_{9}SO, requiring a molecular weight of 549.

The infra-red spectra of the initial material and recrystallised
Compound XIV (nujol mull).

Compound XV (nujol mull).
fractions, showed that on recrystallisation a carbonyl band at 1760 cm\(^{-1}\) appeared. Three N-H stretching bands, a sharp nitrile band and a strong aromatic band at 765 cm\(^{-1}\) were the predominant assignable bands

(Fig. 1).

The elemental microanalysis figures together with the molecular weight determination indicated that the product isolated contained a maximum of one thiophene ring system and probably three isoindoline residues. Furthermore, the three prominent N-H stretching bands in the infra-red spectrum suggested that the initially isolated product was not cyclic.

In a further experiment the reactant ratios were altered to 3:1 in favour of the imidine, the reaction was otherwise carried out as before, but now the yield of yellow product was 71%. Thorough washing of this material under nitrogen and drying gave a material C\(_{30}\)H\(_{16}\)N\(_{10}\)S, with a molecular weight from mass spectrometry of 548. The infra-red spectrum showed complete absence of carbonyl absorption at 1760 cm\(^{-1}\), but an otherwise similar spectrum to that of the previously mentioned product (Fig. 1).

The structure of these two products are given as (XIV) and (XV). No direct evidence has been found to indicate which terminal nitrogen undergoes hydrolysis although the general stability of the two unit analogue, from 1 mol. of thiophene and 1 mol. of imidine (Chapter 3), suggests the structure (XV) for the hydrolysis product.

These results suggested that further condensations should be undertaken in which the thiophene component was in excess, to promote reactions leading to 2:2 materials, cyclic or open chain. However, the same products were isolated, even in the presence of a four fold excess
of the thiophene compound.

The same compound (XIV) was found when the reaction mixture (1:1 stoichiometry) was left at room temperature for several weeks.

Several attempts were made to prepare metal macrocycles both from compound (XIV), and by using the starting materials and a metal salt. The latter technique has been used to achieve metal macrocycle syntheses where the metal free compound has not been prepared. 13, 41

Reactions of the first kind gave no macrocyclic or metal-containing species when the uncyclised compound (XIV) was heated under prolonged reflux in ortho-dichlorobenzene or dimethylformamide with anhydrous nickel (II) chloride, mercury (II) acetate, or copper (II) acetate. The partially hydrolysed compound (XV) was the sole product recovered in low yield.

Reactions of the second kind also failed to give any metal complexes. No ammonia was evolved from the reactions using copper and mercuric acetates although a good deal of hydrogen sulphide was. With anhydrous nickel chloride in dimethylformamide solution a considerable quantity of nickel phthalocyanine was formed, identified from its visible spectrum, but no sulphur containing products were isolated.

Subjecting compound (XIV) to thermogravimetric analysis showed a weight loss of 10.5% between 290-300° as a definite step, followed by a gradual weight loss of 40% between 350° and 900°. The application of heat might have been expected to give rise to cyclisation by the evolution of ammonia (a weight loss of approximately 3.3%). The general decomposition above 290° would seem to support
the above findings that cyclisation does not take place to any measurable extent in this system.

In a parallel attempt to distinguish between cyclic and acyclic structures, a condensation of (XIV) with benzaldehyde was carried out at 170° for one hour, and a reaction with morpholine was also attempted, but these gave only the product (XV).

The conditions employed here were in excess of those required to form Schiff's bases (Chapter 3) and N-substitution products, respectively, from similar two unit compounds.

(ii) In another parallel series of experiments 5-tert-butyl-1,3-diiminoisoindoline was used in order to obtain more-soluble products, which should have been easier to investigate. The alkylated imidine was prepared by a synthetic route from ortho-xylene. (XVI) 40, 51

Ortho-xylene was treated with tert-butyl chloride, using ferric chloride as catalyst, in a Friedel-Crafts' alkylation. The exothermic reaction, once initiated, proceeded smoothly with evolution of hydrogen chloride. Distillation of the reaction mixture gave 4-tert-butyl-1,2-dimethylbenzene.

Selective oxidation of the methyl groups was carried out by treatment with an excess of potassium permanganate in boiling aqueous pyridine. Again the reaction was exothermic, no heating being necessary during the addition of permanganate. After work up the solution was acidified with hydrochloric acid precipitating the potassium salt of 4-tert-butyl phthalic acid. Further treatment with concentrated hydrochloric acid gave a mixture of the free acid
5-t-butyl-1,3-diiminoisindoline

XVI
and potassium chloride. The acid/salt mixture was added slowly to hot acetic anhydride. After reaction the inorganic salt was removed by filtration and fractional distillation gave the anhydride, which solidified on cooling.

The anhydride was treated with 0.88 ammonia and heated to 320° to give 4-tert-butyl phthalimide, which solidified on cooling. Stirring of the imide with 0.88 ammonia gave the diamide.

Dehydration of the diamide was achieved by passing phosgene into a pyridine solution. Work up with ice/water and acid and extraction with ether gave 4-tert-butyl phthalonitrile.

The imidine from this dinitrile was prepared by heating with anhydrous ammonia in methanol in a sealed tube. The product was contaminated with traces of the tetra-alkylated phthalocyanine (iii) The reaction of 5-tert-butyl-1,3-diminoisoindoline and 2,5-diamino-3,4-dicyanothiophene under 1:1 stoichiometric conditions was undertaken in a similar fashion to the previously mentioned reactions, using dimethylformamide as solvent and an atmosphere of nitrogen. On heating, ammonia was evolved and the mixture became darkly coloured. When the ammonia evolution had obviously slackened (after one hour), the mixture was cooled but no solid separated out. The removal of the bulk of the solvent and the addition of cold water, however, precipitated an orange solid. Further purification on a chromatographic column using chloroform as eluent gave a mixture, the main fraction of which was isolated as an orange powder, melting point 265°. Further purification by preparative thin layer chromatography gave a sample of composition C_{42}H_{40}N_{10}S and in agreement the
XVII

XVIIA. \( R = \text{Bu}^+ \), \( R' = \text{Bu}^+ \), \( R'' = H \)

XVIIIB. \( R = \text{Bu}^+ \), \( R' = H \), \( R'' = H \)
mass spectrometric molecular weight was 716. The infra-red spectrum of the material showed the presence of N-H, -C=N and -C=NH, and absence of carbonyl groups. It thus appeared that this material was the alkylated analogue of (XIV) having a structure indicated by (XVII).

(iv) Light Absorption Data.

The light absorption spectra of compounds (XIV) and (XV) in 1-chloronaphthalene showed absorption bands at longer wavelengths (416nm and 420nm respectively) than either component, and indeed than the cross-conjugated macrocycles of type (V). The small bathochromic shift shown by (XV) over (XIV) is not readily explicable, the complexity of the molecular system precluding any detailed analysis of the fine structure of these molecules.

Proton Magnetic Resonance Spectra.

The low solubility of the non-alkylated products prevented spectra being recorded in ordinary organic solvents. Spectra were, however, obtained in trifluoroacetic acid (a stronger acid than hydrochloric), in which compound (XIV) was soluble and showed no signs of decomposition. The p.m.r. spectrum showed two ill-resolved signals at 0.95τ and 1.25τ corresponding to one proton each, and two groups of overlapping lines at 1.72τ and 2.00τ corresponding to four and six protons respectively. No other signals were observed in the region -10τ to 10τ with the region -2.0τ to 0.0τ obscured by the solvent absorption. The two low field signals were attributed to protons $H_A$ in (XIV), deshielded by the nitrile groups. The remaining signals corresponded to the four protons $H_{A1}$ (at lower field) and six protons $H_B$ at higher field.

The products bearing alkyl groups were indeed adequately
soluble for p.m.r. examination. A possible complication was positional isomerism in the products making interpretation less easy. For the tri-tert-butyl material (XVII) there are two isomeric structures, arising from two possible reaction sequences (page 35). The first, A, involves formation of a two unit intermediate. This probably has the structure (a) because the imidine can be expected to react preferentially at the 3-position, as previously indicated. Then follow two reactions with the imidine at the 3-positions, resulting in structure (b). The second scheme, B, requires the reaction of the two unit intermediate (a), with a pre-formed intermediate (c), 5-tert-butyl-1-imino-3(5-tert-butyl-1-imino-3-aminoisoindolenine)aminoisoindoline, which would give structure (d).

The p.m.r. spectrum would be expected to show a maximum of six lines arising from the tert-butyl groups in the product, assuming both postulated structures (b) and (d) are present, and the two alkyl groups labelled 1 and 4 would have very similar chemical shifts. If only one structure were present, there would be only three lines. The spectrum of a deuteriochloroform solution showed four lines from tert-butyl groups at 8.50 \( \tau \), 8.56 \( \tau \), 8.60 \( \tau \) and 8.62 \( \tau \) corresponding closely to twenty seven protons. The presence of four lines in the spectrum could only be reconciled with the presence of both products (b) and (d). Possibly the terminal alkyl groups are equivalent in pairs.

The lowfield region showed a series of low intensity bands from 1.40 \( \tau \) to 2.70 \( \tau \), corresponding to nine protons arising from the benzene rings. A small broadened signal at 3.6 \( \tau \) of two proton intensity was assigned to the NH protons.
Several attempts were made to condense 2,5-diamino-3,4-dicyanothiophene and m-phenylenediamine-di-(1:3-diiminoisoindoline) to form a cross-conjugated macrocycle, without success. Dimethylformamide, n-butanol, and ethanol were employed as solvents giving darkly coloured solids in low yield, showing no distinct melting points. Infra-red spectra showed peaks comparing exactly with those of the reactants and no cyclic products were isolated from these reaction mixtures.

The findings outlined above would seem to conflict with those of Von G. Manecke and D. Wohrle, in that they claim a macrocyclic structure of the type already outlined (XIII), containing two sulphur atoms in the central ring. From the above results it can be seen that even in the most favourable of circumstances the "linear" compound, containing only one sulphur residue, shows no evidence of cyclisation. Two related reasons why this should be so can be suggested. Firstly, molecular overcrowding arising from the presence of the bulky sulphur atom would tend to force the ring systems on either side above and below the plane of the thiophene ring, preventing the close approach of the terminal reactive groups. A molecular model of the expected macrocycle can be made but requires considerable strain on the component parts and shows severe buckling of the ring. Secondly, the geometry of the thiophene ring is such that the amino groups on either side, in the 2 and 5 positions, are close to a linear orientation, with respect to each other. A scale drawing, assuming a flat molecule, shows that this geometry tends to position the terminal groups away from each other, again restricting the possibility of cyclisation, Fig.2.
A self condensation reaction of 2,5-diamino-3,4-dicyano-thiophene in liquid ammonia was discovered (Chapter 7), but no evidence was obtained for the formation of a cyclic product.

It appears that the small geometrical differences between the pyrrole and thiophene ring systems (Fig.3) resulting from the greater atomic size of sulphur as compared with nitrogen, are sufficient to prevent macrocycle formation.

The lack of reactivity of the "linear" product (XIV) towards benzaldehyde and morpholine is disconcerting. A possible explanation is that the molecule is not in fact linear but is folded, as in the scale drawing, such that the terminal nitrogen atoms are "inaccessible" towards reagents. The unsuccessful attempts to ring-close $m$-phenylene-diamine-di-(1:3-diiminoisoindoline) (VII) with the diamino thiophene seem to support the view that the geometry of the thiophene is incorrect for its incorporation in macrocycles of the porphyrin type.
During the attempts to condense 1,3-diiminoisoindoline and 2,5-diamino-3,4-dicyanothiophene, it was found that the latter compound was appreciably soluble in 2-methoxyethanol. Hence this solvent was used as an alternative to dimethylformamide, being less likely to react with any products formed.

A reaction with 1:1 proportions of imidine and diamine gave, after four hours (under reflux in nitrogen), a yellow solid, sparingly soluble in most organic solvents. Extraction of this solid with boiling pyridine gave two fractions, one insoluble in pyridine and another sparingly soluble in hot pyridine. The latter fraction was recrystallised repeatedly from nitrobenzene to give ultimately fine needles of a tan-coloured solid, \( C_{14}H_{8}N_{5} \). The product decomposed above 300° without melting. The insoluble fraction appeared to be a mixture of compounds and further work up was discontinued.

The tan-coloured compound showed a molecular ion (the most abundant peak in the mass spectrum) of \( m/e \) 292 and a paucity of fragment ions, indicating high thermal stability. The two major fragment ions occurred at \( m/e \) 164, corresponding to the thiophene ring system, and \( m/e \) 129 corresponding to the isoindole system. Thus the major fragments arise from cleavage of the molecule into its two components.

The infra-red spectrum (Fig.4) showed the presence of \( N-H, 3430, 3360, 3250 \text{ cm}^{-1} \), \( C=N, 2210 \text{ cm}^{-1} \) and an ortho-disubstituted benzene ring, 770 \text{ cm}^{-1}.

The product was identified as the 1:1 condensation product, and so was either 1-imino-3-(5-amino-3,4-dicyanothiényl)imino isoindoline (XVIII) or its tautomer as indicated.
Compound XVIII (nujol mull).

Compound XXII (nujol mull).
The p.m.r. spectrum (dimethylsulphoxide solution) showed a multiplet of signals from 1.4 to 2.6, from six protons and a broadened singlet at 3.41, from two. The latter signal resembles that at 3.25 arising from the amino groups of the parent thiophene compound.

The availability of this 2-unit compound, albeit in rather low yield, prompted an attempt at its self condensation, in the expectation of forming the 2:2 macrocycle, as in related cases. Reaction in refluxing dimethylformamide, rapidly produced the previously encountered yellow product (XIV). Thus disproportionation and recombination must have occurred, as noted in some other cases.

The compound (XVIII) in ethanolic solution showed no reaction towards n-butylamine, aniline or morpholine, even on prolonged heating, and only the starting material was recovered. This seems strange in view of the fact that 1-imino-3-phenyliminoisoindoline, a close analogue, condenses readily with a further mol. of a primary amine.

In order to gain further information about the reactivities of the terminal functional groups, (XVIII) was treated with benzaldehyde. The diaminothiophene was already known to produce a Schiff's base. Either one molecular proportion of benzaldehyde would condense to give (XIX), or two molecular proportions of aldehyde might condense to give (XX).

(ii) The reaction with benzaldehyde was carried out under conditions as used for the parent diaminothiophene, i.e., heating to 160-170° in neat benzaldehyde for twenty minutes, followed by heating to the same temperature with an equal volume of nitrobenzene. It was considered afterwards that this last stage might have effected a dehydrogenation rather than dehydration.
Following the above procedure a bright yellow crystalline product was obtained, which could be sublimed (with some decomposition) above 315°C. The composition was \( \text{C}_{28}\text{H}_{16}\text{N}_{6}\text{SO} \), corresponding to neither of the expected structures (XIX) and (XX). Mass spectrometry revealed a molecular ion of m/e 484 and isotopic peaks satisfying the formula above. The major fragment ions showed loss of CO (m/e 456, m* 429.6), \( \text{C}_6\text{H}_5 \) (m/e 407, m* 342.3), \( \text{C}_6\text{H}_5\text{CO} \) (m/e 379), OH (m/e 467) and \( \text{C}_6\text{H}_5\text{CONH} \) (m/e 364), where m* represents a metastable peak arising from the particular fragmentation. The infra-red spectrum (Fig. 5) showed a single absorption band at 3300 cm\(^{-1}\) (NH), a sharp band at 2240 cm\(^{-1}\) (C=N), a strong band at 1670 cm\(^{-1}\) (R-N-CO-R) and four strong bands at 770, 765, 710, 685 cm\(^{-1}\) (aromatic).

Thus the molecule contained two benzaldehyde residues from which an oxygen atom was not eliminated as water. A possible structure appeared to be (XXII), derived from the addition product (XXI) by dehydrogenation. This could have been effected by either the benzaldehyde or the nitrobenzene.

The p.m.r. spectrum (\( \text{N}-\text{methyl-2-pyrrolidone} \) solution) showed a broadened singlet at \(-1.70 \tau\), of one proton intensity, a sharp singlet at 0.85\( \tau \) of one proton intensity, and a multiplet of many lines between 1.25\( \tau \) and 2.60\( \tau \) from fourteen protons. The singlet at 0.85\( \tau \) is assigned to the methine proton (structure XXII), possibly deshielded by the nitrile group (the similarly positioned methine protons of 2,5-bis-(benzylideneamino)-3,4-dicyanothiophene show a singlet at 1.02\( \tau \)). The broadened lowfield singlet is assigned to the NH proton possibly at lowfield due to hydrogen bonding with the oxygen atom. The addition of deuterium oxide to the solution caused the loss of this lowfield
XXI OXIDANT → NC CN + REDUCED OXIDANT

(a)

(b)
signal as would be expected.

To assist in the p.m.r. assignments, attempts were made to obtain analogues from p-substituted benzaldehydes. Only p-dimethylaminobenzaldehyde gave a low yield of a product, m.p. 285°, with the composition C_{23}H_{17}N_5S. This was supported by mass spectrometry, a molecular ion of m/e 423 being observed. The new product could be either (A, page 47) or (B), with the former structure being more likely, particularly because of the ease of condensation of the parent diaminothiophene with p-dimethylaminobenzaldehyde.\(^{48}\)

The isolation and characterisation of these aldehyde products prompted model experiments with diiminoisoindoline and o xo isoindoline (Chapter 4). The compound (C, page 47), (prepared from 1-imino-3-oxoisoindoline and the diaminothiophene), was also reacted with benzaldehyde and a product, identified as (\textit{D}), was isolated. This gave a molecular ion of m/e 381. The insolubility of the compounds (\textit{C}) and (\textit{D}) was such that p.m.r. spectra could not readily be obtained. In dimethylsulphoxide solution, (\textit{C}) showed only a very broadened multiplet 1.4\(\tau\) to 3.4\(\tau\), and a small broadened singlet at 3.6\(\tau\). The broadened signals in this spectrum may reflect the general difficulties of purification encountered for this compound.

(iii) Light Absorption Data

The light absorption spectra for the above compounds are in close agreement with results previously reported for analogous diiminoisoindoline and oxo isoindoline derivatives.\(^{6}\)

\begin{align*}
| \text{(XVIII)} | \lambda_{\text{max}} | \text{DMF} | e \\
| \text{ } | 300\text{nm} | 355\text{nm} | 9,100 | 9,700 \\
\end{align*}
(XXII) $\lambda_{\text{max}}$ 388nm 407(sh) 433 438
chlorobenzene e 11,400 10,400 5,900 5,600

(C) $\lambda_{\text{max}}$ 342nm
DMF e 10,500

(D) $\lambda_{\text{max}}$ 348nm 398(sh) 417(sh)
1-chloronaphthalene e 5,900 4,500 4,000

The introduction of the thiophene ring system onto diiminooisoindoline causes a bathochromic shift, giving rise to a maximum wavelength absorption band at 355nm (XVIII), closely paralleling that found in 1-imino-3-phenyliminoisoindoline in both position, 360nm, and intensity. The use of oxoisoindoline in place of diiminooisoindoline (C) gives rise to a hypsochromic shift to 342nm.

The anils (XXII) and (D) show absorption maxima at 458 and 417 nm respectively, at longer wavelengths than their precursors, reflecting the considerably increased extent of conjugation in both compounds. The bands correspond, furthermore, to that found for 2,5-bis(benzylideneamino)-3,4-dicyanothiophene of 426 nm. The somewhat longer-wavelength band shown by (XXII) 1-benzoylimino-3-(5-benzylideneamino-3,4-dicyanothienyl) iminoisoindoline (438 nm) accords with there being more extended conjugation in this product, perhaps arising from a contribution from the more conjugated structure (XXIIb).

The lack of reactivity of(XVIII)towards primary amines and morpholine is unusual for this type of compound since analogous compounds have readily undergone reaction under comparable or milder conditions.6
CHAPTER 4
In the process of identifying the anomalous compound from the condensation of 1-amino-3-(5-amino-3,4-dicyanothienyl) iminoisindoline and benzaldehyde, a synthesis was considered that should have led by an unambiguous route, to the dianil \( \text{XX} \). It was hoped to form a monoanil from diiminoisindoline and benzaldehyde \( \text{XXIII} \), and then react the terminal imino function with 2,5-diamino-3,4-dicyanothiophene to give \( \text{XXIV} \). A further condensation with benzaldehyde would then give the required dianil \( \text{XX} \).

Thus 1,3-diiminoisindoline was heated, in neat benzaldehyde, under similar conditions to those employed previously. The reaction mixture rapidly became very darkly coloured. Addition of a small quantity of dry benzene to the cooled reaction mixture gave a mass of fine, darkly coloured crystals. Repeated recrystallisation of this material from dry benzene gave long, fine white needles resembling cotton wool. During the early purification stages the strongly coloured impurities could be largely filtered off from the benzene solution: the visible spectrum in 1-chloronaphthalene suggested that the material was largely phthalocyanine. The white crystalline material showed a melting point of 211-212°C, and gave microanalytical figures corresponding to \( \text{C}_{22}\text{H}_{17}\text{N}_3\text{O} \). A series of thin layer chromatography experiments using silica and alumina stationary phases showed only one component. A mass spectrum confirmed the elemental analysis in giving a molecular ion of \( m/e \) 339. The infra-red spectrum showed a single band at 3260 cm\(^{-1}\) (N-H), three weak bands at 3040 cm\(^{-1}\) (Ar-H), 2950 and 2850 cm\(^{-1}\) (C-H), three strong bands at 1720 cm\(^{-1}\), 1620 cm\(^{-1}\),
1640 cm\(^{-1}\), as well as aromatic bands in the 650-800 cm\(^{-1}\) region.

Standing the solid in the presence of deuterium oxide for several days, followed by thorough drying, caused the N-H band at 3260 cm\(^{-1}\) to diminish and a new band at 2440 cm\(^{-1}\) (N-D) to appear. The exchange was clearly incomplete. No other changes were observed in the spectrum of the partially deuterated sample.

An acid hydrolysis experiment, using aqueous hydrochloric acid, gave phthalimide (74.7% of the calculated quantity), and a small quantity of benzaldehyde, isolated as its 2,4-dinitrophenylhydrazone.

All this evidence suggested the following possible structures (XXV-XXVIII), of which two, (XXV) and (XXVII) are tautomers.

The same compound was isolated from a reaction in chlorobenzene, though in lower yield. No reaction was found in chloroform solution, even after twenty four hours under reflux.

An experiment was carried out using para-dimethylaminobenzaldehyde and diiminoisoindoline, but the very large amount of phthalo-cyanine formed completely spoiled attempts to isolate an analogous product.

A condensation of 1-imino-3-oxoisoindoline and benzaldehyde, under the above conditions gave, on work up, a pale blue crystalline product. Several recrystallisations from both ethanol and benzene successively, gave fine white needles showing a melting point of 212-213\(^{\circ}\). Elemental microanalysis indicated the composition C\(_{15}\)H\(_{12}\)N\(_2\)O, confirmed by mass spectrometry, giving a molecular ion of m/e 236. The infra-red spectrum of this material was closely similar to that from the imidine, showing a single band at 3260 cm\(^{-1}\) (N-H), moved by deuteration to 2430 cm\(^{-1}\), and strong bands at 1720 cm\(^{-1}\) and 1660 cm\(^{-1}\).
These results could be fitted to three structures having some resemblance to those above, and again two, (XXIX) and (XXXI), are tautomers. The p.m.r. spectra of the two compounds provided useful structural evidence. That of the diiminoisoindoline product in deuteriochloroform solution showed a multiplet of lines 1.70-2.70 ppm corresponding to fifteen protons, a singlet at 3.70 ppm of one proton, and a broadened singlet at 4.80 ppm of one proton intensity. The addition of deuterium oxide to the deuteriochloroform solution considerably sharpened the signal at 4.78 ppm, and left the singlet at 3.70 ppm unchanged as well as the multiplet unchanged, except for a reduction in intensity to approximately fourteen protons, (Fig. 6).

The addition of trifluoroacetic acid to the deuteriochloroform solution again sharpened the broad peak and moved it downfield to 4.54 ppm. The other signal was unchanged in shape but moved downfield to 1.30-2.65 ppm, and its intensity corresponded to eighteen protons, (Fig. 7).

Clearly from the above data, structure (XXVI) is untenable since no methylene signal is observed in the p.m.r. spectrum. The effect of deuterium oxide or trifluoroacetic acid on the spectrum clearly indicates that the exchangeable N-H proton is coupled weakly to another proton, and hence structure (XXV) can be dismissed. Both the remaining possibilities would be expected to show spectra similar to that actually found and no decision as to which is correct can be made on the basis of the p.m.r. spectrum alone. It can be argued that the carbonyl function in (XXVII), because of inhibition of amide resonance, should give a higher frequency absorption in the i.r. than the normal amide carbonyl in (XXVIII). The band at 1720 cm$^{-1}$
Compound XXVII in deuteriochloroform solution, the offset represents the addition of a small quantity of D$_2$O.

Compound XXVII in deuteriochloroform solution with a trace of trifluoroacetic acid.
Compound XXVII (nujol mull).

Compound XXXII (nujol mull).
would therefore appear to support the former structure.

The spectrum of the oxoisoindoline adduct in deuteriochloroform shows a multiplet at 1.90-2.75 \( \tau \) of ten protons, a sharp singlet at 3.68 \( \tau \) of one proton, and a broadened singlet at 4.78 \( \tau \) of one proton intensity. The addition of deuterium oxide sharpened up the peak at 4.77 \( \tau \), and left the other signals unchanged except for a slight reduction in intensity of the multiplet. Thus structure (XXX) can be disregarded since no methylene signal is observed. Similarly structure (XXXI) is again untenable since the exchangeable proton is remote from \( H_a \). Hence structure (XXIX) seems to be the correct assignment from p.m.r. evidence, which correlates with that of the infra-red spectrum.

The similarity in the resonance spectra of both adducts is not surprising since they have closely analogous structures. In both compounds the sharp singlet at 3.70 \( \tau \) and 3.68 \( \tau \), is attributed to the methine proton \( H_b \), showing no interaction with any other protons. The broad signal at 4.78 \( \tau \) and 4.77 \( \tau \) is attributed to \( H_a \), broadened because of coupling with \( N-H_c \), a phenomenon observed in other compounds containing this grouping.\(^{54}\)

The \( N-H_c \) signal lies under the aromatic multiplet as indicated by a reduction in intensity on deuteration. The chemical shift of this proton would at first sight seem to be rather high compared to that found in diiminoisoindoline (1.24 \( \tau \)) and oxoisoindoline (0.05 \( \tau \)). From the configuration of structures (XXVII) and (XXIX), however, it can be observed that this proton lies above the carbon-nitrogen double bond and hence would be expected to suffer a degree of shielding relative to the two reference compounds referred to above.
(ii) In a parallel study, a condensation of diiminoisoindoline with deuterobenzaldehyde was undertaken to obtain further structural evidence.

N-Methylbenzanilide, prepared from N-methylaniline and benzoyl chloride, was reduced with lithium aluminium deuteride in dry ether to give α-deuterobenzaldehyde. This material was characterised by the infra-red spectrum which showed the C-D absorption and no absorption due to C-H.

Reaction of this sample with diiminoisoindoline under the previous conditions gave a small quantity of deuterated product (30mg). The p.m.r. spectrum of this material in deuteriochloroform showed only the multiplet at 1.8-2.77. There was no trace of either singlet. Thus the protons $H_a$ and $H_b$ in structure (XXVII) had both been replaced by deuterium. This demonstrated that $H_a$ was indeed derived from the aldehyde function, presumably through a hydride transfer process.

Several attempts were made to prepare derivatives of these compounds, to substantiate further the structures proposed. The labile N-H group seemed the obvious point of focus. Thus reactions were attempted with methyl iodide in acetone, methyl iodide under pressure, diazomethane, ethylene oxide, benzoyl chloride in pyridine and phenyl isocyanate. No derivatives were obtained using the above reagents, perhaps because insufficiently vigorous conditions were used.

A reaction of the imidine product (XXVII) with acetic anhydride under reflux gave a small quantity of a white crystalline product, $C_{24}H_{19}N_2O_2$. This molecular composition was confirmed by a mass spectrum showing a parent ion of m/e 381, forty-two mass units above that of the parent molecule. The infra-red spectrum showed the
absence of bands above 3000 cm\(^{-1}\) and the presence of a new strong band at 1680 cm\(^{-1}\) assignable to (\(\text{N}-\text{CO.CH}_{3}\)).

The p.m.r. spectrum of this acetylated material in carbon tetrachloride solution, showed an extended multiplet \(1.80-3.30\ \tau\) of many lines, prominent in which was a sharp doublet centred at \(3.15\ \tau\). A very small spike occurred at \(3.85\ \tau\) of low intensity. The total relative intensity of these low-field signals corresponded closely to sixteen protons. Two singlets at \(7.65\ \tau\) and \(6.45\ \tau\) occurred, of total relative intensity of three protons. The latter two singlets were in the ratio of approximately four to one respectively, (Fig.10).

The structure assigned to this product was that of (XXXII), the \(\text{NH}\) having been acetylated. The presence of an adjacent tetrahedral carbon atom and a comparatively bulky benzylideneamino group allowed two distinct configurations (a) and (b). The presence of two singlets arising from the methyl group supported this conclusion, the acetyl group in (a) being shielded by the \(\text{C} = \text{N}\) bond of the benzylideneamino group compared to that in (b). That the two configurations were not present in equal proportions indicated some stereospecificity towards acetylation.

Two signals were not, however, observed from the \(\text{NH}\) proton in the parent compound (XXVI). The \(\text{N-H}\) proton was known to be comparatively labile and the change from one configuration to the other would be expected to be rapid. A reduction in the temperature at which the spectra were recorded (34\(^\circ\) approximately) might have "frozen" out the two forms. The products, however, were not soluble enough at lower temperatures to permit attempts to observe this phenomenon. The broadening of the signal arising from \(\text{H}_a\) in the parent acetyl may well be
contributed to by the change from one configuration to the other.

The observation of two comparatively intense sharp singlets in the aromatic multiplet region of the acetyl material suggested the non-equivalence of two phenyl groups. The intense doublet observed for these groups has moved to higher field with respect to the parent compound and may reflect the two environments of the benzylideneamino phenyl group.

The protons $H_a$ and $H_b$ were not observed in the acetyl material presumably due to the deshielding effect of the carbonyl group placing them under the extended multiplet. A low intensity singlet at 3.67 ppm was assigned to the less shielded proton $H_a$ in form (XXXIIIa), being more remote from the influence of the carbonyl group than that in (XXXIIIb).

The N-acetyl analogue of the oxoisoindoline adduct (XXIX), showed very similar characteristics to those discussed above for (XXXII). Again two peaks at 7.62 ppm and 8.45 ppm arising from the $-\text{COCH}_3$ group were observed, in the relative proportion of 2.5:1.

During the structural investigation of these products several possible open-chain structures were considered. Accordingly some of the likely and available open-chain precursors were reacted under the above conditions with benzaldehyde. Thus $\text{g-cyanobenzamide}$, phthalonitrile and phthalimide were tried but showed no reaction, and were recovered unchanged.

(iii) Two model compounds which were of some interest in this study were considered to be 1-imino-3-benzoyliminoisoindoline and 1,3-dibenzoyliminoisoindoline. A reaction of diiminoisoindoline and
Fig. 10

Compound XXXII in carbon tetrachloride solution

Fig. 11

Compound XXXIV in deuteriochloroform solution
benzoyl chloride in carefully dried pyridine, at room temperature, gave a crystalline compound of elemental composition $C_{22}H_{15}N_3O_2$, and molecular weight from mass spectrometry of 353. The infra-red spectrum showed a single N-H band at 3380 cm$^{-1}$ and two strong carbonyl bands at 1690 cm$^{-1}$ and 1680 cm$^{-1}$.

The interpretation of the p.m.r. spectrum indicated structure (XXXIV), and proved comparatively straightforward due to the high symmetry of the molecule. A single broadened peak at -1.85$\tau$ was assigned to the N-H proton, which was completely removed on the addition of deuterium oxide. The low field at which this signal occurred was considered as arising from hydrogen bonding with the carbonyl groups, both groups seemingly having equal opportunity of taking part.

A series of sharp bands from 1.50$\tau$ to 2.70$\tau$, corresponding to fourteen protons and no other signals were observed. The total aromatic signal could be broken down into the following assignments. A close approximation to a double doublet centered at 1.65$\tau$ and of four proton intensity arises from the $H_A$ protons which are deshielded by the carbonyl groups. Two five-lined multiplets at 2.02$\tau$ and 2.40$\tau$ are assigned to $H_B$ and $H_C$ protons. The second branch of this signal is partially covered by the signal at 2.65$\tau$ of six protons, and eight observable lines, arising from the $H_D$ and $H_E$ protons, (Fig.11).

The dibenzoyl derivative confirmed the infra-red assignment of the $R_N.CO.R$ grouping found in the benzaldehyde adducts. The p.m.r. spectrum, however, was considerably simplified by the molecule having a high degree of symmetry, and hence no direct comparison with the previous compounds was possible. The mono benzoyl derivative would have been more useful both from a synthetic and spectroscopic point
XXXIV
of view but time precluded an attempt to prepare this compound.

(iv) **Light Absorption Data.**

From the infra-red and p.m.r. evidence the molecular structures given as (XXVII), (XXIX) and (XXXII) would appear best. The u.v. light absorption data (for ethanol) provided supporting evidence:

![Chemical structure](image)

<table>
<thead>
<tr>
<th></th>
<th>(\lambda_{\text{max}})</th>
<th>e</th>
<th>(\lambda_{\text{max}})</th>
<th>e</th>
</tr>
</thead>
<tbody>
<tr>
<td>R=(\text{N.CO} \text{Ph})</td>
<td>219 (\text{nm})</td>
<td>48500</td>
<td>220</td>
<td>47000</td>
</tr>
<tr>
<td>(R^1=\text{H})</td>
<td>251</td>
<td>16200</td>
<td>247</td>
<td>16500</td>
</tr>
<tr>
<td></td>
<td>295</td>
<td>6500</td>
<td>258(sh)</td>
<td>13600</td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>6200</td>
<td>300</td>
<td>7000</td>
</tr>
</tbody>
</table>

\[
\begin{array}{c|c|c|c|c|c}
\hline
\lambda_{\text{max}} & e & \lambda_{\text{max}} & e \\
\hline
\text{R=0} & 219 & 36500 & 222 & 26900 \\
\text{R}^1=\text{H} & 251 & 13800 & 248 & 9400 \\
\text{R=0} & 297 & 4600 & 257(sh) & 7700 \\
\text{R}^1=\text{H} & 305 & 4500 & 302 & 3800 \\
\hline
\end{array}
\]

\[
\begin{array}{c|c|c|c|c|c|c}
\hline
\lambda_{\text{max}} & e & \lambda_{\text{max}} & e \\
\hline
230 & 248 & 255(sh) & 284 & 297 & 309 & 331 & 350(sh) \\
23100 & 20800 & 18860 & 18000 & 20600 & 22600 & 19600 & 10500 \\
\hline
\end{array}
\]

The considerable body of evidence gathered on the fine structure of diiminoisoindoline and its derivatives, has previously been referred to (Chapter I). By comparing many fixed-bonded structures using simple derivatives it has been possible to demonstrate that iminoisoindoline type compounds (A) show absorption maxima at shorter wavelengths than the aminoisindolenine type compounds (B). In the oxo series of the
type exemplified by (A) maxima around 302 nm were observed whilst the type (B) structures showed maxima around 343 nm. In the corresponding imino series the type (A) compounds exhibit maxima between 302-320 nm and type (B) from 368-379 nm.

From the data reported above the maximum absorption occurs at 305 nm, which would seem to favour the iminoisoindoline type structure. The long wavelength absorption bands present in the dibenzoyl derivative suggest a contribution from a form more conjugated than (XXXIV). The prototropic shift illustrated would give a more highly (page 64) conjugated form with little or no displacement of atoms comprising the "hydrogen bonded" ring. That this shift does not occur slowly to any great extent, at least in deuteriochloroform, is indicated by the high degree of symmetry found in the p.m.r. signals. This does not of course preclude a very rapid change from one form to another.

(v) Discussion

The mechanism by which the benzaldehyde products are formed
is clarified slightly by the experiment using deuterated benzaldehyde. The stoichiometry of the reaction products requires, at some stage a hydride transfer, which can be represented in the following scheme, using deuterated aldehyde. The initial addition of 1,3-diiminoisoindoline and benzaldehyde, will give intermediate \( \text{A/B} \) and water. The latter, in the presence of the imidine as a strong base may give the reducing ion \( \overset{\text{O}}{\text{Ph.C-D}} \), an ion postulated as taking part in the Cannizzaro reaction.\(^{56, 57}\) The hydride transfer is envisaged as taking place in order to reduce the strain in the unsaturated, fused-5-membered ring and give \( \text{D} \).

The intermediate \( \text{D} \) can then react thermally with benzoic acid to give the amide (XXVII) which was the product isolated. Of two other schemes for the formation of (XXVII), one suggests that benzoic acid is a second product, and the other that benzyl alcohol should arise. However, these products were not detected by chromatographic techniques. Hence the above simple scheme is favoured.

A similar scheme can be written for conversion of the oxo compound into (XXIX). It is to be noted that the products were obtained in low yield, phthalocyanine formation predominating.

It would be of considerable interest to use deuterated imidine and 2-methyl-1,3-diiminoisoindoline under these conditions, since the p.m.r. spectra of the anticipated products would provide further evidence as to the validity of the assignments made. The methyl derivative would also determine whether or not the second stage, \( \text{D} \) to \( \text{E} \), proceeds via reaction with benzaldehyde or benzoic acid.
PhCDO + H₂O + IMIDINE  (as base) → Ph

(Base,H)⁺

XXVII
Several attempts were made to prepare analogous derivatives using 1-imino-3-thioisoindoline, and 1-phenyliminoisoindoline in place of the imidine, and also with furfural in place of benzaldehyde, without however any success. It is not immediately clear why no products were formed.

A number of Schiff's bases of guanazoles (Chapter 6) were prepared using similar conditions to those above. The potential imidine type structure of these compounds might have been expected to show similar characteristics towards aromatic aldehydes as those of 1,3-diimino and 1-imino-3-oxoisoindoline. The products isolated, however, were the expected simple anils.
CHAPTER 5
Chapter 5.

(i) A preparation of guanazole (3,5-diimino-1,2,4-tetrahydrotriazole) was first attempted using the reactants and conditions as described in the earliest reported preparation, from hydrazine hydrochloride and dicyandiamide at 106° in a sealed tube. Only the starting materials were isolated, however, from the reaction mixture and further attempts to use this method were abandoned in favour of an easier synthesis. This subsequent method, from dicyandiamide and hydrazine hydrate at 70°, described by R. Stolle and K. Krauch, gave the authentic material in reasonable yield.

A similar procedure was used in the preparation of 1-phenylguanazole (1-phenyl-3,5-diimino-1,2,4-triazolidine) from dicyandiamide and phenylhydrazine hydrochloride as described more recently by Steck, Brundage and Fletcher.

The preparation of 1,2-dimethylguanazole (1,2-dimethyl-3,5-diimino-1,2,4-triazolidine) was envisaged from N,N'-dimethylhydrazine dihydrochloride and dicyandiamide under similar conditions to those described above. The preparation of the symmetrical hydrazine derivative was that described in the literature. Hydrazine hydrate was dibenzoylated, using benzoyl chloride in aqueous alkali. The dibenzoyl compound was dimethylated, using dimethylsulphate and the resulting dibenzoyldimethyl hydrazine was acid-hydrolysed to give N,N'-dimethylhydrazine dihydrochloride and benzoic acid, the latter being removed by steam distillation.

An initial attempt at preparing the dimethyl triazole derivative was carried out with dicyandiamide and a slight excess of substituted
hydrazine salt, in water under reflux conditions. No reaction took place, the starting materials only being recovered. Using similar reactant proportions and heating to 100-105° for four hours in a sealed tube, gave long transparent needles of the substituted guanazole hydrochloride monohydrate. Thermogravimetric analysis showed loss of water at 50-80° followed by loss of hydrogen chloride from 150-200° and decomposition of the free base from 240°. The base itself was isolated by neutralisation and repeated recrystallisation from alcohol.

(ii) Several attempts were made to react guanazole and 1-phenylguanazole with aniline, The idea being that if aniline condensed with the guanazole, acting the part of an imidine, then there would be the possibility of macrocycle formation with m-phenylenediamine. No reaction took place with aniline, after reflux periods of four to twenty two hours.

With stoichiometric proportions of diiminooisoindoline and guanazole, however, in boiling 2-methoxyethanol or ethanol, reaction took place readily with the evolution of ammonia and formation of a brown solid. After four hours the heating was stopped and the solid product isolated as a brown powder showing no melting point up to 400° but decomposing above 370°. A mass spectrum of this material showed the presence of abundant ions at m/e 227, m/e 335 and m/e 420, corresponding to the two, three and four unit materials (G, H, XXXV respectively ). The mixture proved intractable as far as fractionation was concerned being only sparingly soluble in boiling organic solvents. Repeated Soxhlet extraction with methanol or chlorobenzene resulted in the formation of the oxo compounds of (G) and (H) and the loss of (XXXV ).
Soxhlet Extraction With
Methanol or Chlorobenzene
Similar findings were made with 1-phenylguanazole and diiminoisoindoline, again giving a yellow-brown powdery solid sparingly soluble in organic solvents. Mass spectrometry showed the presence of the two unit compound (m/e 303), the three unit compound (m/e 431) and the macrocycle (m/e 572), as well as a small amount of higher molecular weight material.

With dimethylguanazole and diiminoisoindoline again an insoluble brown powdery solid was formed. The mass spectrum showed the presence of the two and three unit materials at m/e 256 and m/e 383 and no higher molecular weight materials. The product was moderately soluble in boiling methanol, but repeated crystallisation failed to provide a workable system for separation, the components presumably being of similar polarity.

From the above experiments it was clear that, in the case of guanazole and 1-phenylguanazole at least, macrocycle formation was possible, although the reaction conditions used were insufficiently vigorous to give only the macrocycle. The separation of the components from the above mixtures was likely to be very difficult due to the low solubilities and the similarities of the products.

A condensation of guanazole and diiminoisoindoline was carried out in boiling n-butanol over a period of twenty two hours. The precipitated brown solid was filtered off, washed with ethanol and dried in vacuo at 80°. Mass spectrometry gave a molecular ion of m/e 420. Elemental nitrogen analysis fitted substantially the formula \( \text{C}_{20}\text{H}_{12}\text{N}_{12} \). The infra-red spectrum showed two bands at 3280 cm\(^{-1}\) and 3140 cm\(^{-1}\) (NH), as well as prominent bands at 1685 and 1660 cm\(^{-1}\) (C=\text{N}) and 760 cm\(^{-1}\) (aromatic). The product was sparingly soluble in organic solvents,
XXXV

XXXVI

$R = \text{H OR PHENYL}$
though soluble enough in pyridine and 1-chloronaphthalene for measurement of the light absorption spectrum. The maximum wavelength absorption occurred at 397 nm as a shoulder to a more intense band at 373 nm. These maxima are rather higher than the analogous pyridine macrocycle and its analogues, though of reduced intensity. The product was soluble in concentrated sulphuric acid and anhydrous trifluoroacetic acid without any apparent decomposition, giving red-brown coloured solutions. Thermogravimetric analysis showed a 5.0% weight loss from 210-330°C followed by a 68.5% loss from 330-850°C. The p.m.r. spectrum in trifluoroacetic acid showed two sets of five lines centred at 1.58τ and 1.90τ. The structure assigned to this compound was that of (XXXV), the 2:2 macrocycle.

Analogous interaction of 1-phenylguanazole and diiminoisoindoline in boiling butanol for seven hours gave a brown powdery solid, C_{32}H_{20}N_{12} (M 572). Mass spectrometry supported this composition by showing a molecular ion of m/e 572. The infra-red spectrum showed similarities to the analogous guanazole compound except for the presence of a sharp band at 3305 cm^{-1} (NH) and a strong band at 755 cm^{-1}, arising from the phenyl groups. The compound was sparingly soluble in organic solvents but sufficiently so in pyridine for measurement of light absorption, and in trifluoroacetic acid for the p.m.r. spectrum. The light absorption in pyridine showed similarities to that of the guanazole product, in that there were bands at 394 nm, and 372 nm but there were also two very weak bands at the longer wavelengths of 518 nm and 550nm. The p.m.r. spectrum showed multiplets centred at 1.90τ (four protons) and 2.25τ (fourteen protons). Thermogravimetric analysis showed a 61.2% weight loss from 280-610°C. The structure assigned to this
compound was that of (XXXVI, R=Ph, M=2H) the 2:2 macrocyclic product.

(iii) To overcome the solubility problem encountered with the above
macrocyycles recourse was made to the use of 5-tert-butyl-1,3-diimino-
isoindoline.

Thus guanazole and the alkylated imidine were heated under
reflux in 2-methoxyethanol for eight hours, affording a 90% yield of
a yellow-brown solid, \( \text{C}_{28}\text{H}_{28}\text{N}_{12} \). The infra-red spectrum was similar
to that found for the non-alkylated compound except for the appearance
of a series of sharp bands at 2890 and 2950 cm\(^{-1}\) ( aromatic \( \text{C-H} \)), 3030 cm\(^{-1}\)
(aromatic \( \text{C-H} \)) and 3140, 3280 cm\(^{-1}\) (NH). The light absorption spectrum
in dimethylformamide was very close to that of the non-alkylated compound
in both intensities and band positions. The p.m.r. spectrum in tri-
fluoroacetic acid showed two small peaks of a multiplet, of unequal
intensity, centred at 1.54 and 1.80 from six protons, and a sharp
singlet at 8.48 from eighteen protons. The product was probably a
mixture of the two positional isomers ( S ) and ( T ), these arising by the alternative reaction pathways (A) and (B)
which are a result of the fact that the alkylated imidine condenses
with amines preferentially at the 3 position. The environments of the
tert-butyl groups in the two isomeric macrocycles do not differ app-
reciably and so there is only a single \( \text{t-butyl} \) p.m.r. signal from
them.

The analogous reaction of 1-phenylguanazole and 5-\( \text{t-butyl-}
1,3-diiminoisoindoline gave a similar brown powdery solid separated
by thin layer chromatography on alumina into two components, a non-
mobile yellow-brown fraction and a bright blue, highly mobile fraction.
From a chromatographic column the highly mobile component was separated.
R = GUANAZOLE RESIDUE
off using chloroform, and identified spectroscopically as tetra-\( t \)-butyl phthalocyanine.\(^4\) The quantity was very small indeed. The remaining material on the column proved \( n \) mobile with a variety of solvents and even with dimethylformamide moved only very slowly. Hence the top portion of the column was cut out and extracted with hot dimethylformamide from which a small quantity of brown solid, melting point 245-250°, was obtained. Elemental analysis gave 
\[ C_{40}H_{36}N_{12} \], which was supported by the mass spectrometric molecular weight of 684. The infra-red spectrum showed a general similarity to the non-alkylated macrocycle, except for additional prominent bands at 2860cm\(^{-1}\) and 2960cm\(^{-1}\) due to the alkyl groups. The light absorption spectrum in ethanol showed a wavelength maximum at 354nm, somewhat lower than that for the non-alkylated material in pyridine solution. The material was evidently a mixture of the positional isomers (XXXVII A-E). The p.m.r. spectrum in trifluoroacetic acid showed a weak multiplet at 1.45-2.14\( \gamma \) from six protons, a broadened singlet at 2.22\( \gamma \) from ten protons and an unsymmetrical triplet, at 8.53\( \gamma \), 8.57\( \gamma \) and 8.63\( \gamma \), from eighteen protons. The approximate ratio of the intensities (from peak height) was 1.6:1.0:1.0.

The presence of the additional phenyl groups provides additional anisotropy to the environments of the alkyl groups and some degree of difference in the chemical shifts of these groups is to be expected. Assuming there is little influence of the \( t \)-butyl groups on each other (as seems likely since the analogous spectrum for the guanazole macrocycle showed only a single sharp peak for the same isomeric arrangements) then there appear to be three comparatively distinct environments for the \( t \)-butyl groups, labelled respectively
XXXVII C

XXXVII D

XXXVII E

\[ a \ R' = a \ R'' = \text{-(CH}_3\text{)}_3\text{C} - \quad = b \ R'' = b \ R''' \]

\[ R'' = R''' = H \quad = R' = R'' \]
(a), (b) and (c). Assuming there is an equal population of the five possible structures the numbers of the \textit{t}-butyl groups of different types will be $5a + 3b + 2c$, a relative proportion of $1.7:1.0:0.7$, which does seem to correlate with those found.

The two alkylated metal free macrocycles described above share the common property of low solubility in organic solvents and a high melting or decomposition point. This is rather unusual since the introduction of tert-butyl groups generally increases the solubility of aza-linked macrocycles to a very marked extent. It is suggested that the insolubility arises from the strong intermolecular attractive forces resulting from the many nitrogen atoms present. The substitution of the benzenoid rings by a bulky group does not appear sufficient to overcome this attraction, which must have its strongest effect in the vicinity of the triazole rings. The introduction of the N-phenyl groups reduces the lattice energy such that the compound now shows a distinct melting point before thermal decomposition takes place, but the solubility is only slightly greater than the parent macrocycle and still requires the very powerful solvents dimethylsulphoxide and N-methyl-2-pyrrolidone for dissolution.
(iv) In a preliminary experiment guanazole, diiminoisoindoline and nickel chloride were heated together under reflux in ethanol for six hours. The darkly coloured solid product was heavily contaminated with nickel phthalocyanine and a separation of any other products was not carried out.

An analogous reaction of guanazole, imidine and nickel (II) acetate (hydrated), in ethanol, gave a blue-brown powder in good yield which showed no melting point up to 350°. Analysis gave C_{20}H_{10}N_{12}Ni.2H_{2}O, and two molecules of water were lost at 50° under vacuum, to leave the anhydrous compound, C_{20}H_{10}N_{12}Ni. The nickel estimation gave a consistently high result, possibly due to occluded nickel salt. Thermogravimetric analysis of the anhydrous material showed a general weight loss from 300-800° of 45%. The infra-red spectrum of the hydrate showed a spectrum similar to that of the guanazole metal-free macrocycle (XXXV). In the visible region (in pyridine solution) there was a new peak at 422 nm and a series of shoulders at longer wavelength and of lower intensity than those found for the metal-free macrocycle.

A similar compound was prepared, again in good yield, from 1-phenylguanazole, diiminoisoindoline and hydrated nickel (II) acetate. After drying at 90° under vacuum the product was obtained as a dark brown powder with the composition C_{32}H_{18}N_{12}Ni.H_{2}O. The mass spectrum showed a molecular ion of m/e 628 corresponding to a composition \(^{12}C_{32}H_{18}\text{Ni}^{14}N_{12}\text{Ni}^{58}Ni\). and expected isotopic abundance peaks at 629 and 630. Further drying gave the anhydrous compound C_{32}H_{18}N_{12}Ni, of which a thermogravimetric analysis showed two weight loss steps of 3.3% (180-230°) and 3.5% (230-250°) followed by a loss of 43% due to a general decomposition (300-1000°). The infra-red spectrum of the hydrate
was similar to that of the metal free macrocycle. The visible spectrum (pyridine solution) again showed longer wavelength lower intensity bands compared to the metal free compound.

From the above evidence it was concluded that these two compounds were the nickel complexes of the respective macrocycles, of similar type to that of the pyridine macrocycle (Chapter 1).

Metal complexes were readily formed from these guanazole macrocycles. Of the guanazole macrocycle (XXXV), the Cu(II), Co(II), Zn(II) and Hg(II) complexes were prepared, and of the phenyl-guanazole macrocycle those from Cu(II), Co(II) and Hg(II). All the metal chelates were prepared from the metal acetates, and all were initially isolated as hydrates.

The metal complexes were isolated as powders ranging in colour from dark brown to brick red and yellow, and were generally insoluble in organic solvents except pyridine, in which most were sparingly soluble.

The infra-red spectra of the complexes were all very similar (Tables 1 and 2, Experimental Section page 153).

With the exception of the two mercury complexes, the light absorption spectra of the metal complexes in pyridine solution showed lower intensity, longer wavelength bands than the metal-free precursors. In 1-chloronaphthalene the bands were generally weaker (Tables 3 and 4, Experimental Section page 155).
Light absorption spectra of guanazole macrocycles in pyridine solution.

* Dimethylformamide solution
macrocycles in pyridine solution.

- $\text{MeH}_2$
- t-butyl $\text{MeH}_2$
- $\text{MeCu}$
- $\text{MeMI} \cdot \text{H}_2\text{O}$
- $\text{MnCo} \cdot \text{H}_2\text{O}$
- $\text{MeHg} \cdot \text{H}_2\text{O}$

* Ethanol solution
Magnetic properties of complexes and metal free macrocycles.

The magnetic moments of the macrocyclic complexes of Ni, Cu and Co were determined by the Gouy method. The nickel complexes both showed paramagnetism although the effective magnetic moments were considerably below those expected for complexes with a single unpaired electron (2.80-3.50 BM), the values 0.7 BM and 1.4 BM being found for the guanazole and 1-phenylguanazole macrocycles respectively. The complexes of Ni$^{2+}$ are expected to show either diamagnetism from the square planar configuration or paramagnetism from the octahedral and tetrahedral configurations. Nickel(II) phthalocyanine shows diamagnetism and the square planar configuration of the metal has been verified by X-ray analysis. By analogy it would be expected that the guanazole series would also be square planar. The small magnetic moments arising from these complexes may be caused by the presence of some octrahedral hydrate, since the determinations were made on the initially isolated hydrates.

The magnetic moments of the copper complexes show values close to that reported for the analogous phthalocyanine of 1.75 BM. The guanazole copper (II) macrocycle dihydrate gave a value of 1.64 BM, whilst that of the phenylguanazole copper (II) macrocycle was found to be 1.86 BM. Unfortunately the magnetic moments of the various d$^9$ states, octahedral, square planar and tetrahedral are not distinguishable, and so the hydrated complex may be octahedral. The anhydrous complex however is almost certainly square planar by analogy with copper (II) phthalocyanine.

The cobalt (II) guanazole macrocycle monohydrate showed a moment of 2.17 BM, a value within the range reported for cobalt (II)
The presence of water, however, may have given rise to a proportion of an octahedral complex, which would show a reduced magnetic moment of 1.75-1.95 BM.

For the calculation of these ion magnetic moments, the correction for the diamagnetic susceptibilities of the ligands were determined experimentally.

Almost all organic molecules exhibit the phenomenon of diamagnetism. In diamagnetic substances a magnetic field induces small circuit currents whose magnetic fields oppose the inducing field. Most diamagnetic molecules are not magnetically isotropic and their measured magnetic susceptibilities are average values relating to the three principal magnetic susceptibilities, directed along mutually perpendicular axes.

About 1910 Pascal found that the molecular susceptibility of a diamagnetic substance is an additive property of its component atoms and bonds. From many measurements he compiled diamagnetic constants for atoms and bonds, which have generally been found to correlate closely with experimental findings.\(^{56}\)

It was subsequently found that for aromatic molecules the experimentally determined values for the average molar diamagnetic susceptibility was different to that calculated from Pascal's constants. This difference, called the exaltation, is small for non-aromatic molecules but relatively large for aromatic compounds.\(^{62}\) For example, using Pascal's constants a value of the molar susceptibility of phthalocyanine can be calculated as \(-233\times10^{-6}\) cgs, whilst the experimentally determined value is \(-290\times10^{-6}\) cgs, a difference of \(57\times10^{-6}\) cgs. This exaltation has been ascribed to the presence of a ring current, present
in conjugated molecules such as phthalocyanine, benzene etc. In a general study of the magnetic susceptibilities of aromatic compounds in 1937, Lonsdale reports the anisotropy of phthalocyanine as nearly fifteen times as great as benzene, from measurements made perpendicular to the plane of the ring. This greatly increased value over benzene is related to the increased number of electrons within a larger diameter ring system.

For the guanazole macrocycle the use of Pascal's constants results in a molar diamagnetic susceptibility of $-173 \times 10^{-6}$ cgs while that found experimentally was $-171 \times 10^{-6}$ cgs. Similarly for the phenyl-guanazole macrocycle the calculated value is $-271 \times 10^{-6}$ cgs, whilst that found by experiment was $-262 \times 10^{-6}$ cgs. Thus to a close approximation the calculated and found values correspond closely, and there is little or no exaltation. The conclusion from these findings is that there is little or no induced ring current present in the macrocycles beyond that found in the benzene rings themselves. This conclusion is supported by the light absorption spectra of the metal free compounds showing only cross conjugation, similar to the pyridine macrocycle (V) and unlike phthalocyanine.
Chapter 6.

(i) During the investigation of the reactions of guanazoles and diiminoisoindoline (Chapter 5) a number of model compounds were prepared using oxoisoindoline and monophenyliminoisoindoline in place of diiminoisoindoline. The oxo group is inert towards amine attack and so only two and possibly three unit materials were expected from the reaction with guanazoles. By employing 1-imino-3-phenyliminoisoindoline, phenylimino analogues were expected, since this compound has only one reactive imino function. The several tautomeric possibilities for the guanazoles were expected to provide complications, particularly in the case of 1-phenylguanazole, where the asymmetric substitution of the triazole ring system should give rise to two isomeric two-unit compounds.

Thus guanazole and oxoisoindoline condensed readily in 2-methoxyethanol; ammonia was evolved and a yellow solid precipitated, which was shown to be a mixture of the two and three-unit compounds (XXXVIII) and (XXXIX) by mass spectrometry. The respective parent ions at m/e 228 and m/e 357 were the most abundant in the spectrum. The mixture proved extremely difficult to separate due to its general insolubility in organic solvents. Repeated recrystallisations from a nitrobenzene : dioxan mixture, however, gave a finely crystalline bright yellow solid with a melting point of 340-342°. From the analysis, the compound was substantially the two-unit material (XXXVII), $C_{10}H_{8}N_{6}O$. The infra-red spectrum showed prominent bands at 3300 and 3190 cm$^{-1}$ (NH), 1740 cm$^{-1}$ (CO), 1650 cm$^{-1}$ (C=N) and 770 cm$^{-1}$. It was not possible to extract the three-unit compound from the mixture.
XXXVIII
m.p 340-342°
λ_max 358 nm (ε 10,000) (DMF)

XXXIX

XL
m.p 297-299°
λ_max 298 (ε 14,600)
350 (ε 24,600) (chlorobenzene)

XLI
m.p 255-258°
λ_max 303 (ε 6200), 345 (ε 12,200) (chlorobenzene)

XLII
A similar condensation of 1-phenylguanazole and oxoisooindoline again gave a yellow crystalline solid, with evolution of ammonia. In this case a fractionation of the solid products was possible by solvent treatment, giving two main components. Extraction with an ethanol : n-butanol mixture (boiling) left an insoluble fraction and afforded a soluble fraction crystallising readily from the hot solvent. The insoluble material was subsequently recrystallised from chlorobenzene to give pale yellow crystals, melting point 297-299°. Analysis indicated C_{24}H_{15}N_{7}O_{2}, a formula confirmed by mass spectrometry. The infra-red spectrum showed two sharp bands at 3360 and 3320 cm\(^{-1}\) (NH), as well as prominent bands at 1755 cm\(^{-1}\) (CO), 1660 cm\(^{-1}\) (C=\(\equiv\)N), 770 and 710 cm\(^{-1}\) (aromatic). The evidence indicated that this product was the three-unit compound (XL ).

The soluble product was isolated and recrystallised from chlorobenzene to give a lemon yellow crystalline material, m.p. 255-258°. Elemental and mass spectrometric analysis indicated C_{16}H_{12}N_{6}O. The infra-red spectrum showed a single broadened band at 3280 cm\(^{-1}\) (NH), with other strong bands at 1735, 1665, 775, 765, and 675 cm\(^{-1}\). The material was identified as a probable mixture of the isomers (XLI ) and (XLII). Two isomeric possibilities exist for this molecule neither of which would be expected to be formed exclusively.

A condensation of guanazole and 1-imino-3-phenyliminoisooindoline(page 94) gave a solid product readily. The infra-red spectrum and elemental analysis, however, indicated a mixture of two products, (XXVIII) and (XLVI ). It appeared, therefore that in this reaction the phenylimino group of the starting material (page 94) was more reactive and readily displaced than the imino group which, however, was susceptible
XLIII
m.p 135-140°
$\lambda_{\text{max}}$ 228($\epsilon_{32,300}$), 304($\epsilon_{II,200}$), 356($\epsilon_{II,500}$)

XLIV
m.p 198-202°
$\lambda_{\text{max}}$ 228($\epsilon_{31,200}$), 260($\epsilon_{20,000}$), 321($\epsilon_{9800}$), 351($\epsilon_{II,500}$)

XLV

1-imino-3-phenyliminoisoindoline
With 1-phenylguanazole and 1-imino-3-phenyliminoisoindoline a solid product was obtained as a brown powder. A chromatographic separation on an alumina column, using chloroform as eluent, gave a main component isolated as a brown powder, m.p. 135-140°. Analysis gave C_{36}H_{25}N_9. The infra-red spectrum showed a single band at 3330 cm\(^{-1}\) (NH), and other strong bands at 1640 cm\(^{-1}\) (C=N), 760 and 690 cm\(^{-1}\) (aromatic). The structure was identified as (XLIII).

From the reaction mixture filtrate of the above reaction there was isolated a further solid product which was purified by recrystallisation from n-butanol giving a yellow crystalline material, m.p. 198-202°. Elemental and mass spectrometric analysis gave C_{22}H_{17}N_7, indicative of the two-unit analogue (XLIV/XLV). The infra-red spectrum showed two strong bands at 3470 and 3320 cm\(^{-1}\) arising from the N-H groups.

The three-unit compound (XLIII) is of interest in that if the terminal \(\text{C}=\text{N}\) groups are cis-related, then there is molecular overcrowding between the terminal rings which will force the two phenyl-iminoisoindoline systems above and below the plane containing the triazole moiety. The light absorption data for (XLIII) and (XLIV/XLV) however, show that there is only a small hypsochromic shift in the longest wavelength bands as compared to 1-imino-3-phenyliminoisoindoline itself (360 nm).6

(ii) A number of reactions of guanazole and phenylguanazole with the aromatic aldehydes, benzaldehyde and p-methoxybenzaldehyde (anisaldehyde) were carried out with a view to obtaining products similar
to those found with diiminisoindoline (Chapter 4). Several mono and
dianils were obtained but these proved to have the simple Schiff's
base structures.

Thus 1-phenylguanazole was heated with benzaldehyde, which
also acted as solvent. On warming the mixture the solid dissolved
giving a clear yellow solution. At 90° a solid was deposited which
redissolved at 140-150°, giving a clear orange coloured solution.
The reaction was continued for a few minutes at 160-170°, then heated
with an equal volume of nitrobenzene to the same temperature. Cooling
of the mixture gave a crystalline solid, m.p. 132-133°. Elemental and
mass spectrometric analysis gave C_{22}H_{17}N_{5}. The infra-red spectrum
showed prominent bands at 1610 cm\(^{-1}\) (C=N) and 765, 690 cm\(^{-1}\) (aromatic).
The dianil structure (XLVII) was assigned to this compound. The pair
of sharp peaks at 0.56\(\tau\) and 0.59\(\tau\) (of equal intensity) in the p.m.r.
spectrum (deuteriochloroform solution), from the two methine protons
can be envisaged as arising from their different environments with
respect to the N-phenyl group. The preferred geometry of the molecule
is likely to be as written, since from molecular model studies it can
be shown that it offers the least sterically hindered configuration.

The first-formed intermediate in the above experiment was
obtained by heating the reactants to 85-95°, on a steam bath.
Isolation and purification gave glistening plates, m.p. 234-236°.
Analysis gave C_{15}H_{13}N_{5}. The infra-red spectrum showed prominent
absorption bands at 3390 and 3350 cm\(^{-1}\) (NH), 1660 cm\(^{-1}\) (C=N), and 760,
690 cm\(^{-1}\) (aromatic). The presence of the N-H bands showed this product
to be the monoanil. Two isomers exist (neglecting tautomerism) repres­
ented as (XLVII) and (XLIX ), neither of which would be expected
XLVII  m.p 132-133°  
\[ \lambda_{\text{max}} 355 (\epsilon_{1100}), 279 (\epsilon_{22600}) \]

\[ \text{(MeOH)} \]

XLVIII  m.p 234-236°  
\[ \lambda_{\text{max}}(\text{EtOH}) 269\text{nm}(\epsilon_{13100}), 322\text{nm}(\epsilon_{10400}) \]

XLIX  m.p 216-218°  
\[ \lambda_{\text{max}}(\text{chlorobenzene}) 350\text{nm}(\epsilon_{8000}) \]

L  m.p 216-218°  
\[ \lambda_{\text{max}}(\text{chlorobenzene}) 350\text{nm}(\epsilon_{8000}) \]

LII  m.p 155-160°  
\[ \lambda_{\text{max}}(\text{n-butanol}) 298\text{sh}(25,200), 322(32,200), 352\text{sh}(27,300) \]

LIII  m.p 240-243°
exclusively. Compound (XLVIII) would be expected to exist only in the configuration (a) in which the benzylideneamino group is trans to the ring N-phenyl group: in the cis-form there would be considerable overlap of the benzylideneamino group with the phenyl substituent. Compound (XLIX) should exist in configurations (b) and (c) both equally likely and the environment of the methine protons would be expected to be very similar, but different from that in(XLVIIIa). In accord, the p.m.r. spectrum (dimethylsulphoxide solution) showed a group of three sharp bands of unequal intensities at 0.92 and 0.96, 0.97. The former line showed the greater intensity (0.5 proton) while the latter two lines were of lower and approximately equal intensity (0.25 proton each).

A similar experiment with guanazole itself and benzaldehyde gave a crystalline solid, m.p. 216-218°. During the course of the reaction a solid separated out at 100-110° and redissolved on further heating. A subsequent reaction carried out at 100° over one hour, gave only the originally isolated product, m.p. and mixed m.p. 216-218°. The infra-red spectra of both preparations showed a single band 3260 cm⁻¹ (NH) as well as prominent bands at 1600 cm⁻¹, 1590 cm⁻¹ and 775, 725, 690 cm⁻¹ (aromatic). Elemental analysis gave C₁₆H₁₄N₅, which was supported by the mass spectrometric molecular weight. The structure of this dianil is represented as (L), with (LI) a likely tautomer.

The use of anisaldehyde with 1-phenylguanazole under the previously employed conditions gave only a dianil, m.p. 155-160°, C₂₄H₂₁N₅O₂. The infra-red spectrum showed the absence of NH absorption.
The structure is given as (LII). The p.m.r. spectrum (dimethylsulphoxide solution) again showed two lowfield sharp peaks at 0.75 and 0.81, of one proton intensity each, corresponding to the two different environments of the methine protons.

Guanazole itself and anisaldehyde, however, gave only a monoanil, C_10H_11N_0, as a yellow crystalline compound m.p. 240-243\degree, whose structure is given as (LIII). The p.m.r. spectrum (dimethylsulphoxide solution) showed a sharp singlet for the methine proton at 1.04.

(iii) It is noteworthy that in the above two series of compounds it can be seen that the more highly substituted is the triazole ring system the lower is the melting point, and usually the higher the solubility in organic solvents. The simple two-unit compound (XXXVII) shows a high melting point of 340-342\degree, approaching the decomposition temperatures of the triazole macrocycles. The effect of substituting a phenyl group on the triazole ring is to lower the melting point to 255-258\degree, and increase the general solubility of the compound.

The high melting points and low solubilities of the guanazole macrocycles presumably arises from their very high nitrogen content giving rise to strong intermolecular forces, resulting in high lattice energies. The substitution on the nitrogen atoms makes these atoms less available (sterically) for long range attraction and so lowers the lattice energy, an effect outwardly shown in higher solubility and lower melting point.
Chapter 7.

(i) In an attempt to prepare 1-(5-amino-3,4-dicyano-2-thienyl)imino-3-oxoisooindoline (C-page4) from 1-imino-3-oxoisooindoline and 2,5-diamino-3,4-dicyanothiophene, a reaction was undertaken in refluxing 2-methoxyethanol. This solvent was chosen since it had originally been used in the preparation of the analogous compound 1-imino-(5-amino-3,4-dicyano-2-thienyl)iminoisoindoline (XVII). Reaction of the above components for twelve hours under reflux, during which time ammonia was given off, gave, on work up, primarily the expected two-unit material. During the work up another product was found and extracted out in chloroform solution. This latter fraction was investigated because of its unusually high solubility in common organic solvents, uncharacteristic of either starting material or previously found simple condensation products.

A small quantity of this soluble material was extracted from the product mixture, with chloroform and chromatographed on thin layer alumina plates. Several components were indicated from the chromatogram, the major fraction (also the most mobile) was cut, extracted and isolated as a bright yellow powdery solid, with a melting point of 197°.

Mass spectrometry indicated a molecular ion of m/e 705, and many fragment ions. The infra-red spectrum showed absorption bands at 3420 cm⁻¹ and 3270 cm⁻¹ (N-H), the complete absence of absorption in the region 2700-1800 cm⁻¹, strong bands at 1740 cm⁻¹ and 1720 cm⁻¹, and many other strong bands in the fingerprint region. The absence of any nitrile band was most unexpected since the material gave a positive test for sulphur and hence retained either the intact thiophene ring
system or at least part of the system, yet the nitrile groups were known to be generally unreactive.

Elemental analysis indicated a composition $\text{C}_36\text{H}_{29}\text{N}_3\text{O}_3\text{S}$, with a calculated molecular weight of 703, in agreement with that found. The very high carbon, hydrogen and oxygen content could not be accounted for in terms of either component and structures involving solvent molecules were considered. The possibility of a simple solvate or molecular complex seemed most unlikely in view of the mode of purification. The high molecular weight, found from mass spectrometry, enabled this idea to be dismissed and indicated that solvent had reacted with the other components.

To confirm this solvent reaction a similar condensation was carried out in 2-ethoxyethanol, under the previously outlined conditions. The work up of the reaction products, again gave a soluble material, which after preparative thin layer chromatography was isolated as a bright-yellow crystalline solid, melting point $172^\circ$, also as previously in low yield.

Mass spectrometry showed a molecular ion of m/e 731, which was twenty-eight mass units higher than for the previous formula, corresponding to two further methylene groups in the molecule. The infrared spectrum of this second compound was very closely similar to the first. Elemental microanalysis corresponded to $\text{C}_{36}\text{H}_{33}\text{N}_3\text{O}_3\text{S}$, which has $M^+ 731$.

The light absorption spectra of these two compounds in chloroform were, as expected, closely similar, with both showing a more extensive degree of conjugation than the two-unit compound (C, page 47), itself showing a maximum wavelength absorption at 342 nm.
The p.m.r. spectra of these products in deuteriochloroform proved informative (Table 5). The first salient feature of the spectra was the presence of a twelve proton aromatic signal demonstrating the presence of three oxoisooindoline residues. Secondly, the spectra showed the presence of two alkoxyethanol residues in each molecule in different environments, since the chemical shifts of the two methyl groups (LIV) and the two ethyl groups (LV) were slightly different. Thirdly, in both compounds the \(-\text{O} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{O}-\) group in one of the alkyl chains was deshielded, while the other retained the chemical shift of that found in the parent alkoxyethanol. Fourthly, both spectra showed three small broadened bands, two of which were very similar in chemical shift, though of different band shape.

The addition of deuterium oxide to the deuteriochloroform solutions caused these last three singlets to be removed completely with no change in the rest of the spectra. The isolation of these deuterated samples and their infra-red spectra showed that the two bands at 3420 cm\(^{-1}\) and 3270 cm\(^{-1}\) (NH) had moved to positions of lower wavenumber (N-D).
The molecular structure of these two materials as evidenced by the data compiled above are given as (LIV) and (LV).

The molecular structure assigned to these compounds readily conforms with the p.m.r. spectra found. The environments of the alkoxyethanol chains are different, and hence they would be expected to show different chemical shifts. The "set" of methylene protons labelled A, lying in the "plane" of the adjacent benzene ring would be expected to be deshielded with respect to the B set of methylene protons, as is found. The alkyl groups R both show a slight and marginally different degree of shielding, with respect to the parent alcohol. Molecular models of these compounds show that the terminal alkyl groups tend to lie above and below the general plane of the molecule, and hence would suffer a shielding influence from the aromatic rings. The B set of methylene protons gives rise to absorption at 6.47 cm⁻¹ and 6.50 cm⁻¹ for the methyl and ethyl derivatives respectively, which compares closely to those of the respective alkoxyethanols.

The bands arising from the N-H protons are rather more difficult to assign due to the many positions, with environmental variations, they can occupy. The two unequally broadened singlets at lowfield are assigned to two protons probably involved in hydrogen bonding. Unfortunately there are a number of possible conformations of the molecules in which this type of bonding can occur, both via the
LIV  \( R = \text{CH}_3 \)
LV  \( R = \text{C}_2\text{H}_5 \)
**TABLE 5**

**P.m.r. spectra in deuteriochloroform solution. (Fig. 12)**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Structure of Signal</th>
<th>Chemical Shift (%)</th>
<th>Integrated Intensity</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$OH</td>
<td>Singlet</td>
<td>6.60</td>
<td>3</td>
<td>CH$_3$O-</td>
</tr>
<tr>
<td></td>
<td>Complex multiplet</td>
<td>6.40</td>
<td>5</td>
<td>-OH</td>
</tr>
<tr>
<td>LIV, R = CH$_3$-</td>
<td>Singlet</td>
<td>6.82</td>
<td>3</td>
<td>Shielded CH$_3$O-</td>
</tr>
<tr>
<td>C$<em>{36}$H$</em>{29}$N$_2$O$_7$S</td>
<td>Singlet</td>
<td>6.71</td>
<td>3</td>
<td>Less shielded CH$_3$O-</td>
</tr>
<tr>
<td></td>
<td>Multiplet*</td>
<td>6.42</td>
<td>4</td>
<td>-OH</td>
</tr>
<tr>
<td></td>
<td>Multiplet*</td>
<td>5.60</td>
<td>4</td>
<td>Deshielded</td>
</tr>
<tr>
<td></td>
<td>Singlet (broad)</td>
<td>3.30</td>
<td>1</td>
<td>N-H</td>
</tr>
<tr>
<td></td>
<td>Multiplet</td>
<td>2.30</td>
<td>12</td>
<td>Aromatic</td>
</tr>
<tr>
<td></td>
<td>Singlet (broad)</td>
<td>-0.85</td>
<td>1</td>
<td>N-H</td>
</tr>
<tr>
<td></td>
<td>Singlet</td>
<td>-1.10</td>
<td>1</td>
<td>N-H</td>
</tr>
</tbody>
</table>

* = Of similar structure.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Structure of Chemical</th>
<th>Integrated Intensity</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CH}_3\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{OH}$</td>
<td>Triplet</td>
<td>8.80</td>
<td>3 $\text{CH}_2\cdot\text{CH}_2$</td>
</tr>
<tr>
<td></td>
<td>Complex</td>
<td>6.40</td>
<td>7 $\text{CH}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$</td>
</tr>
<tr>
<td>$\text{LW}_{\text{R}} = \text{CH}_3\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$</td>
<td>Triplet*</td>
<td>8.97</td>
<td>6 Two differently shielded $\text{CH}_2\cdot\text{CH}_2$ groups</td>
</tr>
<tr>
<td>$\text{C}<em>{36}\text{H}</em>{33}\text{N}<em>{7}\text{O}</em>{7}$</td>
<td>Triplet*</td>
<td>8.95</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>(complex)</td>
<td>6.50</td>
<td>8 $\text{R}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}$- and $\text{R}\cdot\text{CH}_2\cdot\text{O}$-</td>
</tr>
<tr>
<td></td>
<td>Multiplet</td>
<td>5.65</td>
<td>4 Deshielded- $\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}$-</td>
</tr>
<tr>
<td></td>
<td>Singlet (broad)</td>
<td>3.30</td>
<td>1 N-H</td>
</tr>
<tr>
<td></td>
<td>Multiplet</td>
<td>2.30</td>
<td>12 Aromatic</td>
</tr>
<tr>
<td></td>
<td>Singlet (broad)</td>
<td>-0.80</td>
<td>1 N-H</td>
</tr>
<tr>
<td></td>
<td>Singlet</td>
<td>-1.10</td>
<td>1 N-H</td>
</tr>
</tbody>
</table>

* = Superimposed.
Fig. 12

Compound LIV in deuteriochloroform solution.

Fig. 13

Compound LV in deuteriochloroform solution.
oxygen and nitrogen atoms, and possibly through the sulphur also.
The singlet at 3.30 ppm is at considerably higher field than the protons
of oxoisoindoline (0.05 ppm) and is presumably in a considerably shielded
non hydrogen-bonding environment.

The effect on the spectrum of (LV) of increasing the temperature
to 50°C, considerably broadened the singlets
at -0.85, 3.30 ppm, leaving the remaining singlet at -1.10 ppm unchanged.
The remaining signals were unchanged although the two superimposed
triplets became more coincident.

At 10°C, the low field singlets were moved downfield to -1.0 ppm
(broadened singlet) and -1.26 ppm (sharp singlet), and the third broadened
singlet moved again downfield to 2.95 ppm. The aromatic multiplet was largely unchanged in structure and chemical shift. The multiplet at 5.65 ppm was split into a broadened band at 6.30 ppm and a multiplet centred at 6.60 ppm. The superimposed triplets were extended slightly having new central positions of 8.88 ppm and 9.00 ppm.

The general changes that occur on lowering the sample temperature clearly indicate that some conformers are being "frozen" out. The broadening of two of the singlets, arising from increasing the temperature, is probably exchange broadening. The unchanged low field sharp singlet is clearly due to a more firmly hydrogen-bonded proton, not affected in the same way as the other two protons.

The complex non-planar structure of these molecules precludes a detailed assignment of the exchangeable protons, even though all three protons are in non-identical environments.

(ii) In a series of experiments connected with these compounds,
atttempts were made to react 2,5-diamino-3,4-dicyano-piophene,
l-imino-3-oxoisoindoline and l-(5-amino-3,4-dicyano-2-thienyl)imino-3-oxoisoindoline, separately with 2-methoxyethanol. No reaction was found to occur with any one of the three, only starting materials being recovered.

It is concluded that the solvent reaction takes place with the intermediates of type (A,pagell1) and (D) rather than the two and three unit materials (B) and (E). The intermediates (A) and (D) are envisaged as being similar to that found in the reaction of diiminoisoindoline with m-phenylenediamine (VII).

The solvent attack on the nitrile functions closely parallels that found in imino ether formation, giving intermediates of type (F) and (G). The cyclisation of (G) is similar to that found in the formation of five numbered heterocyclic systems from suitable diiminoethers. The formation of this new heterocyclic ring involves the formation of a terminally reactive group which then condenses with a further molecule of oxoisoindoline, to give on elimination of ammonia, the final product.

The presence of a tetrahedral carbon atom with four, different groupings would be expected to give rise to optically active molecules. The formation of this asymmetric centre, during the cyclisation, would not be expected to be stereospecific and would be expected to give rise to a racemic mixture.

The solvent has been depicted as reacting with (D) and (F) successively, and, or with (A) and (F). The intermediates (A) and (D) would be expected to eliminate ammonia to give the aza-linked two and three unit compounds (B) and (E), as are actually found, the former to a greater extent than the latter.
Once the intermediate (G) is formed two reaction pathways leading to the compound (LIV/LV) can be envisaged. Either the intermediate (G) eliminates ammonia to give (I) followed by condensation with oxoisoindoline giving (LIY/LY), or the intermediate (G) ring closes to give (H) which condenses with oxoisoindoline to give (J) and eliminates ammonia to give (LIV/LV).

(iii) The formation of these macromolecules involves the reaction of the nitrile groups on the thiophene ring. These nitrile groups generally show a lack of reactivity, the only reported reaction being the self condensation of Von G.Manecke and D.Wohrle giving polymeric materials. An attempt was made, therefore, to form an imino-ether of the thiophene compound using anhydrous 2-methoxyethanol and dry hydrogen chloride gas. Only the hydrochloride salt of the starting material was, however, obtained.

In a rather more vigorous reaction a condensation with anhydrous ammonia was tried, in a sealed tube, with 2-methoxyethanol, at 100-110° for five hours. A solid product was filtered off and chromatographed on an alumina column using methanol as eluent. The product, after work up, was a light brown crystalline material, decomposing above 270°, but showing no melting point up to 330°. The compound was very soluble in methanol or ethanol, and dimethylsulphoxide.

The infra-red spectrum of this material showed similarities to that of the parent compound, particularly in its simplicity. The whole spectrum from 650-4000 cm⁻¹ consisting of only thirteen absorption bands, prominent of which were those at 3440, 3330, 3230 cm⁻¹ (NH); 2250, 2225 (C≡N); 1650, 1595, 1500 and 1185 cm⁻¹ (F'g, 15).
Product LIV, as nujol mull.

Product LVI (nujol mull).
Elemental microanalysis corresponded to \((\text{C}_6^\text{H}_4^\text{N}_4^\text{S})\)\(\text{n}\), showing no addition of any kind to the parent compound. The light absorption spectrum, however, showed greater complexity than that of the starting material, and a maximum wavelength absorption band considerably higher than the starting material, showing more extended conjugation in this new product.

\[
\begin{array}{c|ccccc}
\text{(C}_6^\text{H}_4^\text{N}_4^\text{S})\text{n} & \lambda_{\text{max}} (\text{nm}) & 244 & 292 & 340 & 397 \\
\text{(methanolic soln.)} & \varepsilon & 595 & 258 & 173 & 230 \\
2,5\text{-diamino-3,4-} & \lambda_{\text{max}} (\text{nm}) & 295 & 325 \\
dicyanothiophene & \varepsilon & 6400 & 3500 \\
\text{(dimethylformamide solution)} & \\
\end{array}
\]

The p.m.r. spectrum in dimethyl sulphoxide solution showed a broad singlet at -2.00\(\tau\), and a singlet at 3.28\(\tau\), of relative intensity approximately one to three. The addition of deuterium oxide to this solution removed these two peaks and greatly increased the intensity of the water band at 6.20\(\tau\).

The structure of this compound is not readily apparent although it is not entirely obscure. The simplest possibility is the case of \(\text{C}_{12}^\text{H}_6^\text{N}_6^\text{S}_2\) which occurs for \(\text{n}=2\). The spectroscopic evidence outlined above indicates only one possible structure for this molecule, viz (LVI) in which the amino group of one thiophene molecule has attacked the nitrile function of another, with the formation of an additional
five-membered heterocyclic aza-linked ring system.

Further complications of this structure are possible with \( n \) equal to three, four and so on. The cyclic macromolecule is dismissed since the empirical formula found does not agree with any net loss of ammonia, as would be so in this case. The polymeric form illustrated is one of several similar structures which can be envisaged. In the polymeric chain, however, there is room for only one nitrile-containing thiophene ring system (ignoring terminal positions), since every aza-linkage formed must correspond to a new five-membered heterocyclic ring being also formed. Thus the presence of the strong nitrile bands in the infra-red spectrum indicate that either the chain is comparatively short and does contain only one nitrile-containing unit or the compound is not polymeric (beyond \( n \) equal to 2,3 or 4).

On the basis of previous work (Chapter 2) it is suggested that the compound \( C_{24}H_{16}N_4S_4 \) is perhaps the more probable \( (n=4) \), it being in agreement with the spectroscopic data, and behaving in a similar fashion with that four unit compound from diiminoisoindoline, in chain termination after three condensations.

An attempt to evaluate a molecular weight by mass spectrometry failed. The spectra obtained, at high temperature, showed a prominent peak at \( m/e 164 \) as expected, and fragment ions at higher molecular weight, \( >300 \). The most prominent peaks observed, however, corresponded to sulphur being eliminated, peaks arising at \( S_4, S_6, S_8 \) etc.

A molecular weight determination by vapour pressure osmometry on methanolic solutions, gave the values of 213 and 217. These values suggested, in the absence of anomalous solvent interaction, a composition of about 70% monomer and 30% dimer, or a greater proportion of monomer and a reduced proportion of trimer, tetramer, etc.
Notes on Experimental Procedures

1. All condensation reactions were carried out under an atmosphere of nitrogen, stirred magnetically, and protected by drying tubes. All solvents were dried and distilled before use.

2. Elemental microanalyses were performed by either, Alfred Bernhardt,
Mikroanalytisches Laboratorium,
5251 Elbach Uber Engelskirchen,
Frits-Pregl-Strasse 14-16,
West Germany.

or,

Microanalytical Services,
Department of Chemistry,
University of Surrey,
Guildford.

3. All melting points are uncorrected.

4. Extinction coefficient values were calculated from the equation,

\[ e = \frac{A}{c \cdot l} \]

where:
- \( e \) = molar extinction coefficient
- \( A \) = absorbance
- \( c \) = molar concentration
- \( l \) = path length in centimetres (1cm cells used throughout).
5. Spectroscopic and other instrumental analyses were performed on the following machines:

(i) Infra-red spectra were recorded as mulls in nujol, hexachlorobutadiene and fluorolube on a Unicam SP 200 or Perkin Elmer 457 machine. The $1601 \text{ cm}^{-1}$ or $1029 \text{ cm}^{-1}$ bands of polystyrene were used as calibrants.

(ii) Ultra-violet and visible light were recorded as solutions on a Unicam SP 800 automatic recording spectrometer.

(iii) Mass spectra were obtained using an A.E.I. MS 12 machine, operating by means of the direct insertion probe.

(iv) Thermogravimetric analyses were carried out on a Stanton thermobalance using nitrogen carrier gas.

(v) Proton magnetic resonance spectra were recorded on a P.E., R10 instrument at 60 MHz or a Varian HA 100 instrument at 100 MHz, at a temperature of $34^\circ$. Spectra were recorded in deuteriochloroform ($\text{CDCl}_3$), dimethylsulphoxide (DMSO), N-methyl-2-pyrrolidone (NMP) and trifluoroacetic acid (TFA), using tetramethylsilane as internal reference. The following abbreviations are used in the text, $s$ = singlet, $d$ = doublet, $t$ = triplet, $q$ = quadruplet, $sx$ = sextuplet, $m$ = multiplet, $b$ = broad, $sh$ = sharp.

6. The calculation of shifts in the wavelength of absorption in the infra-red spectra of deuterated species was carried out
using the following equations and approximations.

The relationship between the wavenumber of the absorption band arising from the bond X-Y in the diatomic molecule XY, and the masses of the relevant atoms is given by,

\[ \nu_{X-Y} = \frac{1}{2} \frac{\pi c}{k} \sqrt{\frac{k}{M_X M_Y / M_X + M_Y}} \]  

where \( \nu \) is the fundamental stretching frequency in reciprocal centimetres, c is the velocity of light, k is the force constant of the bond in question and \( M_X \) and \( M_Y \) the relative masses of X and Y. For a molecule containing an X-H bond where the mass of X is much greater than H and the X-H vibration does not mix with other vibrations, then the following approximation is valid,

\[ M_X >> M_H \text{ then } M_X M_H / M_X + M_H \approx M_X M_H / M_X = M_H \]  

hence \[ \nu_{X-H} = \frac{1}{2} \frac{\pi c}{k} \sqrt{\frac{k}{M_H}} \]  

similarly \[ \nu_{X-D} = \frac{1}{2} \frac{\pi c}{k} \sqrt{\frac{k}{M_D}} \]  

thus providing \[ k_{X-H} \approx k_{X-D} \text{ then } \]

\[ \nu_{X-H} = \frac{1}{2} \frac{\pi c}{k} \sqrt{\frac{k}{M_H}} = \sqrt{\frac{M_D}{M_H}} = \sqrt{2} = 1.414 \]  

\[ \nu_{X-D} = \frac{1}{2} \frac{\pi c}{k} \sqrt{\frac{k}{M_D}} \sqrt{M_H} \]
Thus, providing the molecule is heavy enough, exchanging an X-H bond by an X-D bond should move the absorption frequency to a lower value by an amount approximately equal to \( \frac{1}{1.414} \times \) the original frequency. In practice, the ratio \( \nu_{XH} / \nu_{XD} \) is lower than 1.414 reflecting the mathematical approximations in the relationship.


If a cylindrical specimen is suspended in a non-homogeneous magnetic field with the lower end in the region of maximum field and the upper end in the region of effectively zero field, it can be shown that the gram susceptibility is given by:

\[
X = \frac{Kv + bw}{W} \tag{1}
\]

where
- \( K \) is the volume susceptibility of air (\( = +0.029 \times 10^{-6} \))
- \( v \) is the volume of the specimen
- \( w \) is the force exerted on the specimen by the field
- \( W \) is the weight of the specimen
- \( b \) is a constant involving the dimensions of the specimen and the field strength and is obtained by calibration with a substance of known \( X \).

The apparatus consists of a balance, from which a cylindrical specimen is suspended, and an electromagnet. The specimen and suspension system are surrounded by glass to exclude draughts, and a thermometer is arranged to give the temperature near the specimen. The specimens were introduced in a finely divided powder form into a cylindrical tube, of which the weight, volume and diamagnetic correction were found.
by experiment.

The value of \( b \) used was found by calibration, using finely divided \((\text{Ni en}_3)\text{S}_2\text{O}_3\) of which \( X = 11.04 \times 10^{-6} \) at 20°C (decreasing by approximately \( 0.04 \times 10^{-6} \) per degree C rise) and calculation from equation (1).

All determinations were repeated until two consecutive values agreed to within 1%. Values of \( X \), the gram susceptibility of the substance were calculated, and \( X_m \), the molar susceptibility where \( X_m = \text{Molecular Weight} \times X \). Where the metal complex showed paramagnetism the effective magnetic moment was calculated from the equation,

\[
\mu = 2.84 \sqrt{X_a \cdot T}
\]  
\[\text{---------(2)}\]

where \( T \) is the temperature in degrees absolute

and \( X_a = X_m - X_\perp \)  
\[\text{---------(3)}\]

where \( X_\perp \) is the susceptibility of the ligand which is negative, i.e., diamagnetic.
(ii) 1,3-Diiminoisoindoline

To a stirred mixture of phthalonitrile (67g., redistilled and solidified m.p. 141°) and cooled methanol (400 c.c.), liquid ammonia (150 c.c.) was cautiously added, and the whole then heated in a ceramic-lined autoclave at 90-100° for 4 hrs. The cooled, strongly coloured solution, was filtered free of insoluble material and concentrated under reduced pressure. 1,3-Diiminoisoindoline (45g.) separated out as a green microcrystalline solid. Recrystallisation from methanol-ether (charcoal) gave small colourless prisms (37g.), m.p. 194-195° (becoming green). Lit. value 195°. Overall yield 76%. Molecular ion from mass spectrometry m/e 145. P.m.r. spectrum (DMSO), 1.23 χ(b,s) 1 proton, 2.00 χ(sx) 2 protons, 2.38 χ(sx) 2 protons.

Found : C, 66.03 ; H, 4.87 ; N, 28.88.
Calc. for C₇H₇N₃ : C, 66.20 ; H, 4.91 ; N, 28.90% ; M, 145.

l-imino-3-oxoisoindoline.

A suspension of phthalamide (65.6g.) in acetic anhydride (240g., redistilled, b.p. 138-139°) was heated under reflux for 2 hrs. A clear, straw-coloured solution was eventually obtained which, on cooling, separated out a mass of fine white needles. Filtration of this reaction mixture and washing of the crystalline solid with fresh acetic anhydride (25c.c.) gave o-cyanobenzamide. Recrystallisation from glacial acetic acid, washing with ethanol and drying, gave a white crystalline solid (18.9g.), m.p. 179° then 203°. Yield 33%.

In a 50c.c. round-bottomed flask was placed o-cyanobenzamide (17g.), with a thermometer penetrating into the sample. The flask was then placed in an oil bath and heated to 202°, with the sample
became molten. Cooling this melt gave a solid mass, which on recrystallisation from ethanol gave a white solid, m.p. 201-203°. Lit. Val. 203°. Molecular ion from mass spectrometry m/e 146. P.m.r. spectrum (DMSO), 0.05 s 2 protons, 1.95 do 1 proton, 2.25 m 3 protons.

Found: C, 65.75; H, 4.28; N, 19.36.
Calc. for C₆H₆N₂O: C, 65.60; H, 4.11; N, 19.20%. M, 146.

"m-Phenylenediamine-di-(1:3-diiminoisoindoline)."

1:3-Diiminoisoindoline (14.5g.) was dissolved in warm ethanol, and m-phenylenediamine (5.4g., freshly distilled) was added with shaking and cooling. After standing at room temperature for 48 hrs., the yellow solid product was filtered off, washed with fresh ethanol and dried, (11.6g.), m.p. 151-154° (decomp.) Lit value 154° (decomp). Yield 59%.

Tetracyanoethylene (TCE)

Dibromomalonitrile-potassium bromide complex.

In a 2 l three-necked flask equipped with a stirrer, a dropping funnel, and a thermometer were placed cold water (90c.c.), malonitrile (99g., 1.5 moles, B.D.H. m.p. 31-32°) and potassium bromide (75g., 0.63 mole). The flask was placed in an ice bath, and the stirrer started. When the temperature of the mixture had dropped to 5-10°, bromine (159 c.c., 3.05 moles) was added dropwise over a period of 2.75 hrs. The stirring was continued for a further 2 hrs., while the temperature was maintained at 10°C. The precipitated solid was collected by filtration and washed with ice-cold water (150 c.c.) and sucked dry at the pump. The white powdery product was vacuum dried over P₂O₅ (333g.). Yield 86%
Tetracyanoethylene.

A mixture of the dibromomalonitrile-potassium bromide salt (254g., 0.25 mole) and dry benzene (1 l) was placed in a 2-l three-necked flask fitted with a sealed stirrer and a reflux condenser, protected by a calcium chloride drying tube. The stirrer was started and precipitated copper powder (100g., 1.57g. atoms, B.D.H.) added. The mixture was heated under reflux for 16 hrs. The hot reaction mixture was filtered, by gravity through a fluted filter paper. The heavy solid remaining in the flask was heated under reflux with dry benzene (300 c.c.) for a further 30 minutes. Filtration of the hot mixture was carried out as before. Two aliquots of hot benzene (25 c.c.) were used to wash the precipitate, and were decanted through the filter. The combined filtrates (red-brown colour) were concentrated to about 300c.c., and cooled overnight at 5°. The solid material that crystallised out was filtered off, washed with cold benzene and recrystallised from dry chlorobenzene to give a white crystalline solid (22g.), m.p. 197-199°, sealed capillary tube. Lit. value 197-198°. Yield 36%.

2,5-Diamino-3,4-dicyanothiophene.

A solution of TCNE (12.8g., 0.1 mole) in acetone (150c.c.) and carbon disulphide (150c.c.) was cooled to 0-5° in an ice bath. Through this stirred solution was passed hydrogen sulphide at a moderate rate for about 30 minutes. After a few minutes the solution became cloudy due to the formation of colloidal sulphur. The gas flow was stopped and pyridine (50c.c.) was added in one portion via the condenser while the solution was being stirred. The cloudyness disappeared giving a clear brown coloured solution. The hydrogen sulphide
addition was resumed, and continued for a further 30 minutes, during which time a yellow solid settled out. The gas flow was cut off and the mixture stirred for a further 30 minutes. The solid product was filtered off, washed with acetone (500 c.c.) and sucked dry (13.9 g.). The product was purified by dissolving in a minimum quantity of dimethylformamide, adding a small quantity of activated alumina and filtering off the solution. The filtrate was heated rapidly to 80° on a steam bath and boiling water added quickly when a tan coloured crystalline material separated out. Filtration, washing with acetone and drying in vacuo over calcium chloride gave the final product (11.8 g.), subliming with decomposition above 250°. Molecular ion from mass spectrometry m/e 164. P.m.r. (DMSO), 3.23 γ (s). λ max (dimethylformamide) 295 nm (6400), 325 nm (sh) (3500).

Principal ν max (Nujol) 3460 s, 3380 s, 3260 s, 2220 s, 1620 s, 1570 s, 1535 s, 1400 w, 1355, 1255, 1150, 1010 cm⁻¹.

Found : C, 44.00; H, 2.56; N, 34.07; S, 19.39
Calc. for C₆H₄N₄S : C, 43.89; H, 2.46; N, 34.13; S, 19.55; M, 164.

1,3-Diminoisoindoline and 2,5-diamino-3,4-dicyanothiophene in dimethylformamide solution.

Initial experiments were carried out using a one to one stoichiometric ratio of reactants. Subsequent analysis of the product obtained in this way indicated that a higher yield of product would be obtainable using a three to one ratio of imidine to dianinothiophene.

In a 100 c.c. conical flask equipped for magnetic stirring and fitted with a reflux system, was placed diminoisoindoline (2.18 g.)
and 2,5-diamino-3,4-dicyanothiophene (0.82g., 0.3 mol%). A stream of
dry nitrogen gas was played over the mixture and maintained in this
manner throughout the reaction. Dimethylformamide (40c.c., distilled
from P₂O₅, b.p. 149-150°) was added via the condenser and the reaction
mixture allowed to stand at room temperature for 10 minutes, with
stirring. The mixture was then heated for 15 minutes during which time
much yellow solid separated out with evolution of ammonia. The mixture
was cooled and the solid filtered off, washed with fresh solvent,
acetone and ether, and dried 70°/0.5 mm Hg 6hrs., giving a bright
yellow powdery solid (1.94g.). Yield 71%. Molecular ion from mass
spectrometry m/e 548. λ_max (1-CN) 416 nm (20,000), 400(19,000) 378(20,000).
P.m.r. (TFA), 0.95τ(b,s) 1 proton, 1.25τ(b,s) 1 proton, 1.72τ(m) 4 protons, 2.00τ(m)6 protons.
Principal ν_max (Nujol) 3435, 3330, 3270, 3055, 2225, 2210, 1670,
1635s, 1595s, 1535s, 1460s, 1400s, 1226s, 1015, 965s, 895, 765s, 620cm⁻¹.
Found : C, 65.64 ; H, 3.09 ; N, 25.33 ; S, 5.72.
C₃₀H₁₆N₁₀S requires C, 65.70 ; H, 2.92 ; N, 25.50 ; S, 5.84% ; M,548.
Recrystallisation of this compound from o-dichlorobenzene or dimethyl-
sulphoxide gave a new product, of molecular weight 549.
Principal ν_max (Nujol) 3430, 3330, 3060w, 2230, 1735s, 1550s, 1620,
1595, 1540s, 1460, 1375, 1285, 1085, 1035s, 955, 870, 855, 760s, 705,
680, 645, 630, 615, 605cm⁻¹. λ_max (1-CN) 420nm (13,500), 364 (17,500).
Found : C, 65.37 ; H, 3.31 ; N, 22.63 ; S, 5.86.
C₃₀H₁₅N₉SO requires C, 65.50 ; H, 2.73 ; N, 23.00 ; S, 5.83% ; M,549.
tert-Butyl chloride. 67

Anhydrous tert-butyl alcohol (140g.) and concentrated hydrochloric acid (510c.c.) were shaken together with anhydrous calcium chloride (50g.) for 20 minutes. The lower acid layer was separated off, the halide washed with 5% sodium bicarbonate solution (120c.c.), then water (120c.c.) and dried over calcium chloride. Distillation gave a main fraction, b.p. 50-51° (165g.). Lit. value 49.5-52°. Yield 93%.

4-tert-Butyl-ortho-xylene. 51

Anhydrous ferric chloride (4g.) was added during 30 minutes to a well stirred mixture of ortho-xylene (188.5g.) and tert-butyl chloride (165g., 1.0mol.) at room temperature. After a few minutes a vigorous reaction occurred liberating much hydrogen chloride. A further quantity of tert-butyl chloride (35g.) was then added and the mixture stirred for about 1.5 hrs. The mixture was then heated on a steam bath for 15 minutes with added charcoal and filtered, giving a pale yellow oil. The oil was fractionally distilled giving a bulk fraction, b.p. 209-211°, (171.5g.), nD 1.4985, 1.4988 Lit. value, b.p. 211-212°, nD 1.5002. Yield 60%.

4-tert-Butylphthalic acid and anhydride. 51

Potassium permanganate (360g., 2.25 mols.) was added during 1.5 hrs., to a well stirred boiling solution of 4-tert-butyl-ortho-xylene (81g., 0.5 mol.) in pyridine (500c.c.) and water (1 l). After final refluxing for 45 minutes excess KMnO4 was removed with ethanol (100c.c.), the mixture filtered and the residue washed well with hot water (300c.c.).
The filtrates and washings were distilled to reduce the bulk to about 300c.c., and to remove excess pyridine and 4-tert-butyl-ortho-xylene. Careful addition of concentrated hydrochloric acid precipitated a basic potassium salt of 4-tert-butylphthalic acid, which was collected and stirred with concentrated hydrochloric acid to yield potassium chloride and 4-tert-butylphthalic acid (96g.). The mixture was heated with acetic anhydride (192c.c.) and the yellow coloured solution filtered free of inorganic salt. Distillation of this solution gave a fraction, b.p. 305-310° as a pale yellow liquid solidifying on cooling (35.5g.). Yield 35%.

4-tert-Butylphthalimide and 4-tert-butylphthalamide.

4-tert-butylphthalic anhydride (35.5g.) was heated with aqueous ammonia (d 0.88, 180c.c.) to 325°, to give a clear brown liquid which solidified on cooling to a tan coloured solid. Crystallisation from ethanol gave colourless prisms, m.p. 133-134° of the imide (30g.). Yield 85%.

The imide (10g.) was stirred with aqueous ammonia (d 0.88, 50 c.c.) for 3.5 hrs. at room temperature. The diamide was filtered off as a powdery white solid. Crystallisation from water with a little ethanol gave colourless needles (9.4g.), m.p. 164-165°. Lit. value 165°. Yield 87%.

4-tert-Butylphthalonitrile.

A reaction flask (1 l) was equipped with two wide-bore delivery tubes and an air condenser, from which excess gases could be vented. The flask was charged with 4-tert-butylphthalamide (20g.) and pyridine
(150 c.c.) and the mixture maintained at 80°, while a rapid stream of phosgene was bubbled through the mixture. After a short while the reaction mixture became dark and viscous. Phosgene was passed through the solution for 1.5 hrs. After cooling, small pieces of ice were added to the reaction mixture and the apparatus washed with ice-cold water until gas evolution ceased. Acidification to Congo Red paper was carried out with concentrated hydrochloric acid and the solution continuously extracted with ether for 24 hrs. Evaporation of the ether gave a brown oil, which solidified on cooling and scratching. Recrystallisation from methanol (charcoal) gave 4-tert-butylphthalonitrile as colourless needles (13.4 g.), m.p. 58-59°. Lit. value 59°. Yield 80%.

5-tert-Butyl-1:3-diiminoisoindoline.

4-tert-Butylphthalonitrile (5.0 g.) was dissolved in methanol (25 c.c.) and the solution cooled to -10°. Liquid ammonia (8 c.c.) was added cautiously and the mixture heated in a sealed tube at 116° for 5 hrs. After cooling, the tube was carefully opened and excess ammonia allowed to evaporate. 5-tert-Butyl-1:3-diiminoisoindoline (3.9 g.) was collected. A second crop (0.2 g.) was obtained on reducing the filtrate to half bulk. Recrystallisation from methanol gave the purified imidine, m.p. 205-210° (decomp. from 160°). Yield 75%. \( \lambda_{\text{max}} \) (96% Ethanol) 229, 258, 295, 306 nm.

Found: C, 71.71; H, 7.39; N, 21.02.

Calc. for \( \text{C}_{12}\text{H}_{15}\text{N}_{3} \): C, 71.50; H, 7.49; N, 20.90%.
5-tert-Butyl-1:3-diiminoisoindoline and 2,5-diamino-3,4-dicyanothiophene in dimethylformamide solution.

5-tert-Butyl-1:3-diiminoisoindoline (0.203g.) and 2,5-diamino-3,4-dicyanothiophene (0.165g., 1.0 mol.) were dissolved in dimethylformamide (5c.c., redistilled) and heated under reflux conditions for 1 hr. Evaporation of the bulk of the solvent and the addition of water precipitated a fluffy orange solid (0.340g.). A quantity of this material (0.270g.) was taken up in benzene giving a clear red solution and some insoluble material (tan coloured, 0.04g.). The coloured solution was chromatographed on alumina (CAMAG M.F.C., 100-240 mesh, neutral) using benzene, benzene-ether mixtures as mobile phases, finally eluting with chloroform. Concentration of this solution gave an orange solid (0.06g.). Thin layer chromatography using alumina plates and chloroform-xylene (30:70), and extraction of the bulk component with chloroform gave the orange solid. Final precipitation from dimethylformamide solution with water gave a small quantity of material (38mg.) as an orange solid, m.p. 265°. Molecular weight by mass spectrometry 716.

P.m.r. (CDCl₃) 1.4-2.8 (m) 9 protons, 3.60 (b, s) 2 protons, 8.55 (q) 27 protons. Principal Mₘₐₓ (Nujol) 3450, 3360s, 3240, 2200s, 1620s, 1565s, 1535s, 1430, 1350s, 1060, 1010w, 850w, 795w.


C₄₂H₄₀N₁₀S requires C, 70.37; H, 5.63; N, 19.54%; M, 716.
1:3-Diiminoisoindoline and 2,5-diamino-3,4-dicyanothiophene in 2-methoxyethanol.

To a hot solution of 2,5-diamino-3,4-dicyanothiophene (1.64g.) in 2-methoxyethanol (30c.c., redistilled from K₂CO₃, b.p. 117-120°) under dry nitrogen, was added dropwise over 15 minutes, a solution of diiminoisoindoline (1.45g., 1.0 mol.) in 2-methoxyethanol (30c.c.). After a few minutes a bright yellow solid began separating out, with the evolution of ammonia. Heating was continued for 4 hrs., then the solid was filtered off of the cooled solution, and dried (2.88g.). Extraction of this solid with boiling pyridine gave two main fractions. The bulk fraction, insoluble in boiling pyridine contained several products and was not worked up. The minor fraction, sparingly soluble in hot pyridine was extracted and recrystallised repeatedly from nitrobenzene, to give fine, small needles of a tan coloured solid (0.73g.), showing no distinct melting point but subliming with decomposition above 260°. Yield 25%. Molecular ion m/e 292. P.m.r. (DMSO) 1.80 ℧ (m) 2 protons, 2.00-2.60 ℧ (m) 4 protons, 3.40 ℧ (s) 2 protons.

Principal \( \nu_{\text{max}} \) (Nujol) 3430s, 3360s, 3250s, 2210, 1630s, 1575, 1555, 1530s, 1435s, 1415s, 770s, 680 cm⁻¹.

Found : C, 57.42; H, 2.90; N, 28.57; S, 10.81.

C₁₄H₈N₆S requires C, 57.52; H, 2.76; N, 28.76; S, 10.97%; M, 292.

Condensation of 1-imino-3-(5-amino-3,4-dicyano-2-thienyl) iminoisoindoline and benzaldehyde.

A sample of 1-imino-3-(5-amino-3,4-dicyano-2-thienyl) iminoisoindoline (412mg.) was heated to 160-170° in excess benzaldehyde (20c.c., redistilled). On heating, the solid dissolved giving a clear
solution. After 20 minutes heating an equal volume of nitrobenzene was added and the mixture maintained at 160-170° for a further 20 minutes. Standing of this reaction mixture at room temperature overnight gave a yellow crystalline solid (170 mg.). The sample was recrystallised from chlorobenzene, washed thoroughly with acetone and dried. Yield 25%. Sublimed with decomposition above 315°. Molecular ion m/e 484. P.m.r. (Me2P) -1.70 (b,s) 1 proton, 0.85 (s) 1 proton, 1.25-2.60 (m) 14 protons. Principal ν max (Nujol) 3340s, 2240, 1670s, 1600, 1575s, 1570s, 1530, 1455, 1395s, 1270, 1230, 1170, 770s, 765s, 710s, 685s cm⁻¹.

C₂₈H₁₆N₆OS requires C, 69.38; H, 3.33; N, 17.31%

Condensation of 1-imino-3-(5-amino-3,4-dicyano-2-thienyl)iminoisoindoline and para-dimethylamino-benzaldehyde.

A sample of 1-imino-3-(5-amino-3,4-dicyano-2-thienyl)iminoisoindoline (200 mg.) was heated to 160-170° in the presence of excess para-dimethylaminobenzaldehyde (1.0g.), followed by heating with nitrobenzene and cooling. A small amount of pink solid separated out. Recrystallisation from chlorobenzene, washing and drying gave a pink solid, m.p. 285° (decomposition), (9mg.). Molecular ion by mass spectrometry 423.

Found: C, 64.74; H, 4.02; N, 22.85.
C₂₅H₁₇N₅S requires C, 65.20; H, 4.05; N, 23.17%
1-imino-3-Oxoisoindoline and 2,5-diamino-3,4-dicyanothiophene
in dimethylformamide.

1-imino-3-Oxoisoindoline (1.46g.) and 2,5-diamino-3,4-dicyano-
thiophene (1.64g., 1.0 mol) were heated under reflux in dimethylformamide
(10c.c.), under a nitrogen atmosphere, for 8 hrs., with the evolution
of ammonia. On cooling and working up with ethanol, a tan-coloured
powdery solid was obtained (2.07g.). Recrystallisation from nitrobenzene
gave the solid product, softening at 280° but showing no melting point
up to 340°. Yield 71%. Molecular ion m/e 293. P.m.r. (DMSO), 1.4-3.4 υ
(broad peak, no fine structure, 3.6 υ (b.s)
Principal υ max (Nujol) 3450s, 3350s, 3200s, 2220, 1740, 1650b,s, 1575,
1540s, 1510s, 1420s, 1300s, 1095, 765s, 715 cm$^{-1}$.
Found: C, 57.36; H, 3.39.
C$_{14}$H$_{17}$N$_{5}$S$_{0}$ requires C, 57.33; H, 2.41 ? %; M, 293.

Reaction of 1-(5-amino-3,4-dicyano-2-thienyl) imino-3-oxoisoindoline
and benzaldehyde.

The two unit compound prepared previously (0.68g.) was
heated to 160-170°, for 30 minutes with excess benzaldehyde (l2c.c.),
followed by heating with nitrobenzene for a similar period and temperature.
Cooling overnight and the addition of ether gave a yellow-brown solid
(0.41g). The product was only sparingly soluble in organic solvents
and could not be purified sufficiently for elemental analysis. Mass
spectrometry showed the most abundant ion in the spectrum at m/e381,
being that calculated for (D, page 47, C$_{21}$H$_{11}$N$_{5}$S$_{0}$).
Principal υ max (Nujol) 3220s, 2240, 1625s, 1560s, 1515, 1410, 1030w,
770s, 710 cm$^{-1}$.
Reaction of 1,3-diiminoisoindoline and benzaldehyde.

1,3-Diminoisoindoline (6.0g.) was heated under reflux with excess benzaldehyde (20c.c., freshly distilled under nitrogen) for 10 minutes. The solid rapidly dissolved on the application of heat, giving rise to a strongly coloured (green-blue) solution, becoming almost black at the termination of the reaction. Cooling and the addition of a small quantity of benzene, crystallised out a solid product, which on filtration and washing with benzene gave a grey crystalline product (3.0g.). Repeated recrystallisation from benzene gave white needles, m.p. 209-210° (yellow on melting). Further recrystallisation from either ethanol or acetone raised the melting point to 211-212°. Molecular weight by mass spectrometry m/e 339. P.m.r. (CDCl₃) 1.84-2.74 χ (m) 15 protons, 3.70 χ (s) 1 proton, 4.78 χ (b.s) 1 proton.

Principal v max (Nujol) 3300, 1720s, 1660s, 1640w, 1500w, 1425, 1335, 1325w, 1210, 1160, 995, 970, 780, 755, 720s, 705s.

Thin layer chromatography on alumina and silica showed only one component, SiO₂(CHCl₃) RF 0.45, SiO₂(CH₆) RF 0.42, Al₂O₃(CHCl₃) RF 0.88, Al₂O₃(CH₆) RF 0.29.

Found C, 77.85; H, 5.09; N, 12.21.

C₂₂H₁₇N₃O requires C, 77.85; H, 5.05; N, 12.38%; M, 339.

Acid Hydrolysis.

A sample of the benzaldehyde adduct (108 mg) was heated for 10 minutes on a steam bath, with aqueous 10% v/v hydrochloric acid (5c.c.), when the whole of the product dissolved. Subsequent cooling gave fine colourless needles (35 mg), identified as phthalimide, m.p. and mixed m.p. 230-231° (75% of theoretical value for C₂₂H₁₇N₃O). The aqueous filtrate was distilled and the distillate treated w. n an ethanolic
solution of 2,4-dinitrophenylhydrazine (30 c.c. of a saturated solution) giving an orange precipitate of benzaldehyde 2,4 DNPH, m.p. 235-236°. Lit. value 237°. (60 m g.).

Reaction of 1-imino-3-oxoisooindoline and benzaldehyde.

1-imino-3-oxoisooindoline (1.09 g.) and benzaldehyde (10 c.c.) were heated together, under reflux for 5 minutes. The solid rapidly dissolved on heating and the mixture became a progressively darker shade of green. Excess benzaldehyde (ca. 5 c.c.) was removed by distillation under vacuum leaving a viscous mass from which a solid separated out. Filtration and washing gave a pale blue solid, (1.03 g.). Recrystallisation from benzene gave a white crystalline solid, m.p. 204-206°, which on further recrystallisation from benzene gave long fine needles, m.p. 212-213° (green on melting). Molecular ion m/e 236. P.m.r. (CDCl₃) 1.90-2.73 (m) 10 protons, 3.65 (s) 1 proton, 4.78 (b, s) 1 proton. Principal νmax (Nujol) 3300, 1725s, 1660s, 1500w, 1400s, 1355, 1300, 1210, 1150, 970s, 805, 785, 755, 725s, 710s cm⁻¹. Found : C, 76.86; H, 5.22; N, 11.77.

C₁₅H₁₂N₂O requires C, 76.25; H, 5.12; N, 11.86 %; M, 236.

Acetylation of the imidine-benzaldehyde adduct.

The diiminoisooindoline-benzaldehyde compound (XXVII, 1.02 g.) and acetic anhydride (15 c.c.) were heated under reflux conditions for 1.0 hrs. The bulk of solvent was distilled off and the cooled concentrate poured into crushed ice, giving a viscous yellow oil. The ice/water was decanted off leaving a sticky gum. This material was taken up in chloroform (100 c.c.), dried over magnesium sulphate, and evaporated
down to a glassy oil. Subsequent crystallisation of this substance from methanol (charcoal) gave a white crystalline solid (0.50 g.), m.p. 165-168° (green on melting). Molecular ion m/e 381. Yield 45%.
P.m.r. (CCl₄) 1.90-3.00 τ(m), 3.15 τ(d), 3.90 τ(s) 16 protons, 7.64 τ(s) and 8.45 τ(s) 3 protons.
Principal νₘₐₓ (Nujol) 1735s, 1680s, 1665s, 1500, 1405s, 1330s, 1220, 1180, 1090, 1045s, 995, 945s, 845s, 780s, 760s, 735, 705s cm⁻¹.

Found : C, 75.60 ; H, 5.09 ; N, 11.18.

C₂₄H₁₉N₅O₂ requires C, 75.57 ; H, 5.02 ; N, 11.02% ; M, 381.

Acetylation of the oxoisoindoline-benzaldehyde adduct.

The oxoisoindoline-benzaldehyde adduct (1.0g.) and acetic anhydride (11c.c.) were heated under reflux and isolated as above. The crude material was dissolved in methanol, shaken with a small quantity of neutral alumina, filtered and the filtrate volume reduced slowly by evaporation. The resulting white crystalline material was filtered off and dried (0.4g.), m.p, 179-185° (softens before melting turning green on melting). Yield 34%. P.m.r. (CCl₄), 1.83-2.83 τ(m), 3.13 τ(d), 3.87 τ(s) 11 protons, 7.63 τ(s) and 8.45 τ(s) 3 protons.
Principal νₘₐₓ (Nujol) 1740s, 1680s, 1660s, 1500w, 1400s, 1350, 1320s, 1295, 1220, 1210, 1185, 1165, 1045s, 1030s, 990s, 950s, 840s, 785, 755s, 750s, 715s, 705s, 695s cm⁻¹.

1,3-diminoisoindoline and benzoyl chloride in pyridine.

An initial attempt to benzoylate the imidine using freshly distilled reagents gave a mixture of starting material, oxoisoindoline and phthalimide. In a subsequent experiment the benzoyl chloride and
pyridine were very vigorously dried and moisture kept away from the reaction.

To 1,3-diiminoisoindoline (1.0g.) in freshly distilled dry pyridine (5c.c., refluxed over KOH for 1 hr.) was added benzoyl chloride (2c.c., freshly distilled under nitrogen, b.p.194-196°). The reaction (in a stoppered flask) mixture became warm and solidified as a pale yellow solid. After standing at room temperature overnight the solid was filtered off and thoroughly washed with ether, giving pale yellow needles (1.6g.), m.p. 178-180°. Molecular ion m/e 363. Yield 66%.
P.m.r. (CDCl₃) -1.87 (b,s) 1 proton, 1.68 (m, seven observable lines) 4 protons, 2.00 (sx) 2 protons, 2.33 (4 lines observable), 2.41-2.69 (m, 8 observable lines) 8 protons.
Principal ν max (Nujol) 3380, 1645s, 1610s, 1595s, 1580s, 1495, 1455, 1315s, 1280s, 1230s, 1170s, 1090, 1060s, 995s, 980s, 750, 725s, 690s cm⁻¹.
Found : C, 74.68 ; H, 4.43 ; N, 12.04
C₂₂H₁₉N₃O₂ requires C, 74.78 ; H, 4.28 ; N, 11.89 % ; M, 363.

Preparation of deuterated benzaldehyde, C₆H₅CDO⁻

N-Methylaniline (21.4g., 0.2 mol, distilled with a trace of Zn dust, b.p. 189-191°) was dissolved in pyridine (25c.c.). Benzoyl chloride (24.9g., 0.2 mol) in dry benzene (25c.c.) was added to this solution, dropwise over 20 minutes. The stirring was continued for 1.5 hrs., when water (100c.c.) was added, the mixture shaken and the aqueous layer separated off. This aqueous solution was separately extracted with fresh benzene. The combined benzene fractions were pooled and washed with 2N hydrochloric acid (50c.c.x2) followed by water (100c.c.). The benzene layer was dried over sodium sulphate and
distilled under vacuum. The major fraction at 171-173° / 4 mm Hg, was collected as a yellow oil. Lit. value 121° / 1 mm Hg. The oil was taken up in heptane and crystallised to a white solid product, m.p. 60-61.5°, (23.5g.) Yield 63%.

N-Methylbenzanilide (4.22g.) was dissolved in dry ether (20c.c.). To this stirred solution was added, dropwise over 20 minutes, a solution of lithium aluminium deuteride (0.26g., 0.32 mol) in dry ether (30c.c.) whilst the temperature was maintained at 0°. After 3 hrs. stirring, ethyl acetate (7c.c.) was added to destroy any Li AlD₄ remaining, followed by 10% v/v hydrochloric acid to destroy the complex. The ethereal layer was separated off and the aqueous layer extracted with ether (20c.c.x2). The combined ether extracts were washed with 2N hydrochloric acid (20c.c.) then water (20c.c.x2), collected and dried over sodium sulphate. The ether was removed over a steam bath and the residual liquid distilled in vacuo, the bulk fraction b.p. 65-68°/ 14mm Hg being a clear colourless liquid (0.68g.). Lit. value for C₆H₅.CO 69° / 15 mm Hg. The residue was recrystallised from heptane to give unreacted N-methylbenzanilide. Yield on unreacted material 40%.

Principal ν max (Neat liquids)

C₆H₅.CHO. 3100 cm⁻¹ (Ar H), 2830 (-CHO), 2740 (-CHO) νCH = 1.34
C₆H₅.CDO. 3100 cm⁻¹ (Ar H), 2120 (-CDO), 2050 (-CDO) νCD

Reaction of α-deuterobenzaldehyde and diiminoisoindoline.

1,3-Diiminoisoindoline (700mg) was heated with excess deutero-benzaldehyde (0.68g.) for 20 minutes giving a strongly coloured solution. On cooling the solid material was filtered off and recrystallised from
benzene to give a white crystalline solid (30 mg) m.p. 210° (green on melting). P.m.r. (CDCl₃) 1.85-2.71 ṽ(m).
Principal ᵂ max (Nujol) 3350w (NH), 2240w (CD), 1720s, 1660s, 1630, 1520s, 1500, 1340, 1310w, 1215, 1170w, 780, 765, 725s, 720s, 705.

Preparation of l-imino-3-thioisoindoline.

The modified method of Drew and Kelly, of the action of an aqueous ethanolic solution of sodium sulphide saturated with hydrogen sulphide gas, on a suspension of phthalonitrile, gave l-imino-3-thioisoindoline. Purification gave a yield of 12% of golden crystalline product, softening 217-218° (decomp.) Lit. value 218° (decomp.)
P.m.r. (DMSO) -0.71 ṽ(b,s) 2 protons, 1.72-2.44 ṽ(m) 4 protons.

Preparation of l-imino-5-phenyliminoisoindoline

Diiminoisoindoline (5.0g.) and aniline (3.2g.) were heated under reflux in ethanol (30c.c.) for 2.5 hrs. The solid that settled out of solution was filtered off, washed, and dried as a yellow powder (6.0g.), m.p. 201-203° (decomp.). Lit. value 203° (decomp.). Yield 79%.
P.m.r. (DMSO) 1.6 ṽ(b,s) 2 protons, 1.95-3.20 ṽ(m) 9 protons.
Preparation of Guanazole (3,5-diimino-1,2,4-tetrahydrotriazole). 58

Dicyandiamide (20g.) was mixed with hydrazine hydrate (30g.) and the mixture warmed to 65-67°, under a stream of nitrogen. As soon as the temperature of the mixture reached 67° heating was stopped and only reapplied to achieve a temperature of 70°. The dicyandiamide went into solution and a large amount of ammonia was evolved. After 1.75 hrs. the heating was stopped and the bulk of the mixture removed in vacuo, giving a straw coloured viscous oil. Work up of this oil with 80% aqueous ethanol containing a small amount of sodium dithionite gave an almost colourless crystalline solid (8.5g), m.p. 200-203°. Lit. value 203°. Yield 43%. Molecular ion m/e 99. Infra red spectrum identical to that of authentic guanazole, SADTLER collection No.19946.

Preparation of 1-Phenylguanazole (1-phenyl-3,5-diimino-1,2,4-triazolidine). 59

Dicyandiamide (8.4g.) and phenylhydrazine hydrochloride (15.9g.) were dissolved in water (35c.c.), and the mixture heated to 95-110° for 4 hrs., with stirring under a nitrogen atmosphere. After cooling the mixture was basified with 35% w/v sodium hydroxide solution, giving a pink crystalline solid. Recrystallisation from water (charcoal) containing a trace of sodium dithionite, under nitrogen gave pale yellow crystals. Drying in vacuo gave 1-phenylguanazole (12.1g.), m.p. 175-176°. Lit. value 175°. Yield 70%.

Preparation of 1,2-dimethylguanazole (1,2-dimethyl-3,5-diimino-1,2,4-triazolidine).

The route considered for the preparation of this compound
necessitated the preparation of $N,N^1$-dimethylhydrazine.

$N,N^1$-Dibenzoylhydrazine

To a stirred, cold solution of hydrazine sulphate (65g., 0.5 mol.) and sodium hydroxide (46g., 1.2mol.) in water (500c.c.) was added, in a dropping funnel, freshly distilled benzoyl chloride (120c.c., 1.03 mol.). Simultaneously from another dropping funnel was added an aqueous solution of sodium hydroxide (45g., 1.1 mol.). The benzoyl chloride was added over a period of 1.5 hrs., the alkali solution slightly faster. After both additions were complete the mixture was stirred for a further 2 hrs., left overnight, then saturated with CO$_2$. The bulky white solid was filtered off, ground with 50% aqueous acetone and sucked dry at the pump. Recrystallisation from glacial acetic acid and careful drying at 100°/0.5 mm Hg over several days, gave $N,N^1$-dibenzoylhydrazine (101g.), m.p. 245-244°. Lit. value 254-258°. Yield 83%.

$N,N^1$-Dibenzoyl-$N,N^1$-dimethylhydrazine

To a stirred mixture of dibenzoylhydrazine (40g., 0.17 mol.) in water (300c.c.) containing sodium hydroxide (5g., 0.13 mol.) at 90°, was added dimethylsulphate (210c.c., 1.27 mol., purified by standing over potassium carbonate until neutral to Congo Red paper) and 185 c.c. of an aqueous solution of sodium hydroxide (125g. in 250c.c.). The dimethyl sulphate was added in 10c.c. aliquots, the alkali at a rate that maintained the mixture slightly alkaline, over a period of 1.5 hrs. Extraction of the cold reaction mixture with chloroform (400c.c.), drying over sodium sulphate and evaporation of the solvent gave a clear
oil which crystallised on standing (40g.), m.p. 65-75°. Lit. value 77-84°. Yield 87%. 

N,N'-Dimethylhydrazine dihydrochloride.

Dibenzoyldimethylhydrazine (40g., 0.13 mol.) and hydrochloric acid (32% v/v, 200 c.c.) were gently heated under reflux for 2 hrs., when much benzoic acid crystallised out. The benzoic acid was removed by steam distillation and the residual liquor evaporated to dryness under reduced pressure leaving the almost white crystalline product. Recrystallisation from ethanol gave sym-dimethylhydrazine dihydrochloride (9.5g.), m.p. 158-164°. Lit. value 165°. Yield 54%.

N,N'-Dimethylguanazole.

Dicyandiamide (1.68g.) and sym-dimethylhydrazine dihydrochloride (2.93g.) were placed in a sealed tube with water (6c.c.). The tube was heated to 100-105° for 4 hrs. The crystalline solid formed was filtered off and recrystallised several times from dilute aqueous hydrochloric acid, and air dried (1.8g.), m.p. 240°. Yield 46%. Molecular ion from mass spectrometry m/e 127, with prominent peaks at m/e 36 (H^35Cl) and 38 (H^37Cl), m/e 35 (35Cl) and 37 (37Cl). 

Principal ν max (Nujol) 3300s, 3130s, 2140w, 1690s, 1660s, 1630s, 1580s, 1540s, 1460s, 1310, 1230, 1170, 1110, 1090, 920, 750, 740, 710 cm⁻¹.

Found : C, 26.33 ; H, 6.60 ; N, 38.97

C₂H₉N₆.HCl.H₂O requires : C, 26.45 ; H, 6.66 ; N, 38.56 %.

The free base (1.0g.) was obtained by making an aqueous solution of the hydrochloride salt alkaline by the addition of sodium hydroxide solution. The whole was then evaporated to dryness, and the
residue crystallised several times to remove the sodium chloride as insoluble material. The free base was isolated as an off-white solid (0.42 g.). Yield 59%. Molecular ion from mass spectrometry m/e 127, with no peaks at m/e 35, 36, 37 and 38, but with an otherwise identical spectrum to that of the salt.

Guanazole and diiminoisoindoline.

Guanazole (2.97g.) and diiminoisoindoline (4.35g.) were dissolved in hot n-butanol (20c.c.) and heated under reflux, in a nitrogen atmosphere for 22 hrs. Shortly after heating ammonia was evolved and a yellow-brown solid began separating. On cooling, the solid material was collected and thoroughly washed with alcohol and sucked dry at the pump. Drying at 80-90° under vacuum gave a yellow-brown powdery solid (5.7g.), showing no melting point up to 400° but decomposing around 370°. Yield 90%. Molecular ion from mass spectrometry m/e 420. P.m.r. (TFA) 1.45-2.20 \( \tau \) (multiplet of two branches centred at 1.58 and 1.90 \( \tau \) of five observable lines each.)

\[ X = -0.406 \times 10^{-6} \\ X_M = -171 \times 10^{-6} \]

Thermogravimetric analysis showed a 5.0% loss in weight from 210-330° and a 68.5% loss from 330-850° (rapidly from 440-550°).


\( \text{C}_{20}\text{H}_{12}\text{N}_{12} \) requires N, 39.98 %

M, 420.4

1-Phenylguanazole and diiminoisoindoline.

1-Phenylguanazole (5.25g.) and diiminoisoindoline (4.35g.) were dissolved in hot n-butanol (30c.c.) and heated under reflux for 7 hrs., with the evolution of ammonia and the precipitation of an orange-
brown solid. Collection of the solid, washing with alcohol (500c.c.) gave, on drying at 80-90° under vacuum, an orange-brown powdery solid (6.4g.), showing no melting point up to 400°. Yield 76%. Molecular ion from mass spectrometry m/e 572. P.m.r. (TFA) 1.6-3.0 τ(m), two branches centered at 1.90 τ(4 protons) and 2.25 τ(14 protons).

\[ X = -0.449 \times 10^{-6} \quad ; \quad X_M = -262 \times 10^{-6}. \]

Thermogravimetric analysis showed 67.5% weight loss from 280-610°.

Found: C, 66.97; H, 3.66; N, 29.46

C\(_{32}\)H\(_{20}\)N\(_{12}\) requires C, 67.13; H, 3.52; N, 29.35% ; M, 572.6

**Guanazole and 5-tert-butyl-1,3-diminoisoindoline.**

Guanazole (0.20g.) and 5-tert-butyl-1,3-diminoisoindoline (0.41g.) were heated, under reflux, in 2-methoxyethanol (5c.c.) under a nitrogen atmosphere. Initially both materials dissolved to give a clear yellow coloured solution, and then began precipitating a brown solid with the accompanying evolution of ammonia. After 6hrs. the ammonia evolution had slackened and the heating was stopped. Filtration of the cooled mixture proved very difficult due to the very fine particulate nature of the solid. The addition of a little ether however, "granulated", the solid, which was isolated, washed with fresh solvent, then ether and dried giving a yellow-brown powder (0.48g.), showing no distinct melting point but decomposing above 440°. Yield 90%.

P.m.r. (TFA) 1.4-2.0 τ(m), two main peaks of unequal intensity centred at 1.54 and 1.80 τ, 6 protons, 8.48 τ(s) 18 protons.

Found: C, 63.04; H, 5.44; N, 31.36

C\(_{28}\)H\(_{28}\)N\(_{12}\) requires C, 63.14; H, 5.30; N, 31.56%.
1-Phenylguanazole and 5-tert-butyl-1,3-diiminoisoindoline.

1-Phenylguanazole (0.35g.) and tert-butyl diiminoisoindoline (0.40g.) were heated in 2-methoxyethanol (8c.c.), under nitrogen for 8 hrs., with the evolution of ammonia and the formation of a yellow-brown solid. After standing at room temperature for several days this mixture was filtered giving the solid product (0.43g.). Thin layer chromatography on alumina using benzene as mobile phase showed this product to be a mixture of at least two components, (a) a non-mobile yellow coloured component and, (b) a highly mobile component moving with the solvent front and bright blue in colour. The bulk of the preparation was chromatographed on an alumina column using benzene and benzene-chloroform mixtures as eluents. The highly mobile intensely blue coloured material was eluted and found by visible spectroscopy to be largely tetra-t-butyl phthalocyanine (ca 10mg), 338, 604 (sh), 633, 658, 692nm, in 95% ethanol. The non-mobile fraction failed to move with a variety of eluents including methanol and dimethylformamide. The top, sample containing, portion of the column was removed and extracted with boiling dimethylformamide, to give on work up a small quantity of a yellow-brown solid (67 mg), m.p.245-250°, leaving a considerable amount of material adsorbed on the alumina. Mass spectrometry gave a molecular ion of m/e 684 with a low intensity peak at higher molecular weight. P.m.r. (TFA) 1.45-2.14 τ(m) 6 protons, 2.22 τ(s) 10 protons, 8.53 τ, 8.57 τ, 8.63 τ 18 protons.

Found : C, 70.16 ; H, 5.30 ; N, 24.54.

C_{40}H_{36}N_{12} requires C, 70.02 ; H, 5.46 ; N, 24.36% ; M, 584.8
Guanazole, 1,3-diiminoisoindoline and nickel (II) acetate.

Guanazole (1.98g.), 1,3-diiminoisoindoline (2.90g.) and Ni(CH₃C₂O₂)₂·4H₂O (2.49g.) were heated under reflux in ethanol (30c.c.) for 7 hrs. The initially deep yellow-coloured reaction mixture rapidly darkened on heating evolving much ammonia and precipitating an apparently black solid. Cooling and filtration gave a strongly coloured powdery solid insoluble in organic solvents. The solid was Soxhlet extracted with methanol and the residue ground with methanol filtered and sucked dry at the pump, and dried in vacuo (3.64g.), showing no melting point up to 350°. Yield 71% of dihydrate. $X = 0.529 \times 10^{-6}; X_M = 269 \times 10^{-6}$.

Found: C, 47.03; H, 3.46; N, 33.05; Ni, 13.64

$C_{20}H_{10}N_{12}Ni·2H₂O$ requires: C, 46.82; H, 2.75; N, 32.76; Ni, 11.44%.

On drying at 50° under high vacuum the product lost 5.28% of its weight. The calculated value for the loss of two molecules of water being 5.02%, leaving the anhydrous compound,

Found: C, 49.22; H, 2.52.

$C_{20}H_{10}N_{12}Ni$ requires: C, 50.35; H, 2.11%.

Thermogravimetric analysis showed a slow weight loss of 45% from 300-800°, as a single stage.

1-Phenylguanazole, 1,3-diiminoisoindoline and nickel (II) acetate.

1-Phenylguanazole (3.50g.), 1,3-diiminoisoindoline (2.90g.) and Ni(CH₃C₂O₂)₂·4H₂O (2.49g.), were heated in ethanol (30c.c.) under nitrogen for 7 hrs. The copious evolution of ammonia and formation of a strongly coloured solid paralleled the analogous guanazole reactio. The solid was filtered off, ground with methanol, filtered, washed, and dried at 80-90° under vacuum to give a dark brown powder (4.15g.) showing
no melting point up to 350°. Yield of monohydrate 64%.

\[ X = +0.911 \times 10^{-6} ; \ X_M = +605 \times 10^{-6}. \]

Molecular ion from mass spectrometry m/e 628, corresponding to \( \text{C}_{32}\text{H}_{18}\text{N}_{12}\text{Ni} \) with a calculated value of 628.6. The isotope abundance peaks compared favourably with the calculated values,

\[
\begin{align*}
P_{628} & \quad P_{+,1629} & \quad P_{+,2630} \\
\text{Found} & \quad 100\% & \quad 40.9\% & \quad 44.6\% \\
\text{Calculated} & \quad 100\% & \quad 39.2\% & \quad 43.7\%
\end{align*}
\]

\[ \text{C}_{32}\text{H}_{18}\text{N}_{12}\text{Ni}.\text{H}_2\text{O} \text{ requires} \quad \text{C}, \text{ 59.49} ; \ H, \text{ 3.12} ; \ Ni, \text{ 9.10}\%.
\]

Further drying at 90° under high vacuum gave the anhydrous compound.

\[ \text{Found} \quad : \quad \text{C}, \text{ 61.05} ; \ H, \text{ 3.06} ; \ Ni, \text{ 9.06} \]

\[ \text{C}_{32}\text{H}_{18}\text{N}_{12}\text{Ni} \text{ requires} \quad \text{C}, \text{ 61.08} ; \ H, \text{ 2.88} ; \ Ni, \text{ 9.33}\%.
\]

Thermogravimetric analysis showed two distinct weight-loss steps from 180–230° (3.34%) and 230–250° (3.46%) and general decomposition above 300° up to 1000° (36% weight loss).

**Guanazole, diiminoisoindoline and copper (II) acetate.**

Guanazole (1.98g.), 1,3-diiminoisoindoline (2.90g.) and 

\[ \text{Cu} \left( \text{CH}_3\text{CO}_2 \right)_2.\text{H}_2\text{O} (2.00g.) \] were heated in ethanol (20c.c.) as above for 7 hrs., with the evolution of ammonia and formation of strongly coloured solid. Filtration and washing as above gave a dark blue-brown powdery solid (4.5g.). Yield 87% of dihydrate. \[ X = +1.992 \times 10^{-6} ; \ X_M = +959.7 \times 10^{-6} ; \ \mu_{\text{eff}} = 1.64. \]

Thermogravimetric analysis showed weight losses at 70–100° (2%) and 230–800° (35%).
1-Phenylguanazole, diiminoisoindoline and copper (II) acetate.

1-Phenylguanazole (3.50g.), diiminoisoindoline (2.90g.) and Cu(CH₂CO₂)₂.H₂O (2.00g.) were reacted in ethanol for 7 hrs., as previously. The resulting brown solid was isolated washed and dried at 85° under vacuum for several hours (4.6g.) Yield 73%. X = +1.868 x 10⁻⁶; Xₚ = +1185 x 10⁻⁶; μₑffective = 1.84. Thermogravimetric analysis showed 43% weight loss from 260-1000°.

A small quantity of orange-brown solid was recovered from the alcohol washings (0.38g.), identified as metal free macrocycle from its visible spectrum.

Found: C, 60.37; H, 3.05; N, 26.36; Cu, 10.17.
C₂₀H₁₆N₁₂Cu requires C, 60.61; H, 2.86; N, 26.51; Cu, 10.02%.

Guanazole, diiminoisoindoline and cobalt (II) acetate.

Guanazole (1.98g.), 1,3-diiminoisoindoline (2.90g.) and Co(CH₂CO₂)₂, (1.77g.) were heated in ethanol as previously. The brown solid was washed thoroughly with alcohol and dried at 90° under vacuum to give a brown powder (4.2g.). Yield 85%. X = +3.897 x 10⁻⁶; Xₚ = +1930 x 10⁻⁶; μₑffective = 2.25. T.G.A. showed 3.6% loss from 50-100° (calc. value for one molecule H₂O 3.5%) and 51% loss from 300-800°.

Found: C, 48.00; H, 3.26; N, 33.55; Co, 11.97.
C₂₀H₁₀N₁₂Co.H₂O requires C, 48.50; H, 2.44; N, 33.93; Co, 11.90%.
1-Phenylguanazole, diiminoisoindoline and cobalt (II) acetate.

1-Phenylguanazole (3.50g.), diiminoisoindoline (2.90g.) and Co(CH$_3$CO$_2$)$_2$ (1.77g.) were heated in ethanol as above. The brown powdery product isolated after washing and drying amounted to 2.89g. Yield 46% (the solid proved very difficult to filter and isolate and a considerable quantity of material was lost in these processes). $X = +2.386 \times 10^{-6}$; $X_M = +1545 \times 10^{-6}$; $\mu_{\text{eff}} = 2.17$.

Found: C, 60.72; H, 3.09; N, 25.90; Co, 10.08.

C$_{32}$H$_{18}$N$_{12}$Co.H$_2$O requires C, 59.36; H, 3.11; N, 25.96; Co, 9.10%.

Guanazole, diiminoisoindoline and zinc (II) acetate.

Guanazole (1.98g.), diiminoisoindoline (2.90g.) and Zn(CH$_3$CO$_2$)$_2$.2H$_2$O (2.20g.) were reacted in ethanol as previously. The brick red solid obtained after washing and drying amounted to 4.14g. Yield 80%.

Found: C, 46.24; H, 3.52; N, 32.02; Zn, 14.60%.

C$_{20}$H$_{10}$N$_{12}$Zn.2H$_2$O requires C, 46.22; H, 2.69; N, 32.34; Zn, 12.58%.

Guanazole, diiminoisoindoline and mercury (II) acetate.

Guanazole (1.98g.), diiminoisoindoline (2.90g.) and Hg(CH$_3$CO$_2$)$_2$ (3.19g.) were reacted in ethanol as above, giving a red-brown powder (4.61g.). Yield 78%.

Found: C, 36.61; H, 2.57; N, 26.46; Hg, 29.55.

C$_{20}$H$_{10}$N$_{12}$Hg.H$_2$O requires C, 36.86; H, 1.90; N, 26.39; Hg, 31.50%.
1-Phenylguanazole, diiminoisoindoline and mercury (II) acetate.

1-Phenylguanazole (3.50 g.), diiminoisoindoline (2.90 g.) and
Hg(CH$_3$CO$_2$)$_2$ (3.19 g.) were reacted as above, giving a brown powdery solid (5.26 g.). Yield 68%.

Found : C, 47.49; H, 2.84; N, 20.99; Hg, 25.04.

C$_{32}$H$_{18}$N$_{12}$Hg$_2$H$_2$O requires : C, 47.62; H, 2.75; N, 20.82; Hg, 24.85%. 

### Table 1

**Infra-red spectra of guanazole macrocycles as nujol mulls.**

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<th>MoCo₂H₂O</th>
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<td>3300(b)</td>
<td>3300(b)</td>
<td>3270(b)</td>
<td>3270(b)</td>
<td>3280(sh)*</td>
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</table>

*b = broad; w = weak; s = strong; sh = sharp; * = hexachlorobutadiene mull; a = generally weak spectrum; band positions in wavenumbers.*
Table 2

Infra-red spectra of 1-phenylguanazole macrocycles as nujol mulls.

<table>
<thead>
<tr>
<th>McH₂</th>
<th>McNiH₂O</th>
<th>McCu⁺</th>
<th>McCoH₂O</th>
<th>McHg₂H₂O</th>
<th>Di-tert-butyl</th>
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<tr>
<td>330 cm⁻¹</td>
<td>335 cm⁻¹</td>
<td>330 cm⁻¹</td>
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<td>McH₂</td>
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<td>550</td>
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</tr>
<tr>
<td>615</td>
<td>685</td>
<td>685</td>
<td>660</td>
<td>660</td>
<td></td>
</tr>
<tr>
<td>675/680</td>
<td>720/725</td>
<td>715</td>
<td>720</td>
<td>745</td>
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<tr>
<td>755(s)</td>
<td>755(s)</td>
<td>755(s)</td>
<td>755</td>
<td>760</td>
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<td>770</td>
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<td>1015</td>
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<tr>
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<td>1055</td>
<td>1050</td>
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<td>1095</td>
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<tr>
<td>1055</td>
<td>1080</td>
<td>1095</td>
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<td>1130(w)</td>
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<tr>
<td>1195</td>
<td>1195(w)</td>
<td>1195(w)</td>
<td>1190(b)</td>
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<td>1310(w)</td>
<td>1315(w,b)</td>
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<td>3440(w)</td>
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</table>

b = broad;  w = weak;  s = strong;  sh = sharp;  * = hexachlorobutadiene mull;  a = generally weak spectrum;  band positions in wavenumbers.
Table 3
Light absorption spectra of guanazole macrocycles.

<table>
<thead>
<tr>
<th></th>
<th>A MnNi$_2$H$_2$O</th>
<th>B MnCu$_2$H$_2$O</th>
<th>A MnCo$_2$H$_2$O</th>
<th>B MnZn$_2$H$_2$O</th>
<th>A MnHg$_2$H$_2$O</th>
<th>B MnHg$_2$H$_2$O</th>
<th>DMF</th>
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<tr>
<td>$\lambda_{max}$</td>
<td>625(sh)</td>
<td>671</td>
<td>608</td>
<td>515</td>
<td>372</td>
<td>397(sh)</td>
<td>418(sh)</td>
</tr>
<tr>
<td></td>
<td>501(sh)</td>
<td>636(sh)</td>
<td>565</td>
<td>472(sh)</td>
<td>364</td>
<td>373</td>
<td>384</td>
</tr>
<tr>
<td></td>
<td>470(sh)</td>
<td>601(sh)</td>
<td>522(sh)</td>
<td>395</td>
<td>353</td>
<td>364</td>
<td>366</td>
</tr>
<tr>
<td></td>
<td>433(sh)</td>
<td>473(sh)</td>
<td>462(sh)</td>
<td>395</td>
<td>353</td>
<td>364</td>
<td>349</td>
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<tr>
<td></td>
<td>422</td>
<td>425(sh)</td>
<td>434</td>
<td>371(sh)</td>
<td>353</td>
<td>364</td>
<td>332(sh)</td>
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<td></td>
<td>396</td>
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<td>352</td>
<td>335</td>
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<td>343</td>
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<td>3340</td>
<td>1670</td>
<td>3080</td>
<td>397(sh)</td>
<td>418(sh)</td>
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<td>3420</td>
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<td>6600</td>
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<td>5820</td>
<td>12500</td>
<td>12700</td>
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<td>336(sh)</td>
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<td>13900</td>
<td>16300</td>
<td></td>
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</tbody>
</table>

A = Pyridine solution; B = 1-Chloronaphthalene solution;
peak positions in nanometers.
**Table 4**

Light absorption spectra of 1-phenylguanazole macrocycles.

<table>
<thead>
<tr>
<th></th>
<th>A MoNiH₂O λ&lt;sub&gt;max&lt;/sub&gt;</th>
<th>e</th>
<th>411</th>
<th>333(sh)</th>
<th>667</th>
<th>636</th>
<th>560(sh)</th>
<th>510(sh)</th>
<th>445</th>
<th>411</th>
<th>333(sh)</th>
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<tbody>
<tr>
<td></td>
<td>e</td>
<td>1600</td>
<td>740</td>
<td>2280</td>
<td>2750</td>
<td>8400</td>
<td>10200</td>
<td>17900</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>λ&lt;sub&gt;max&lt;/sub&gt;</td>
<td>680</td>
<td>638</td>
<td>588</td>
<td>557</td>
<td>513</td>
<td>450</td>
<td>414</td>
<td>390</td>
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<tr>
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<td>e</td>
<td>2280</td>
<td>960</td>
<td>3560</td>
<td>3680</td>
<td>3860</td>
<td>12300</td>
<td>14200</td>
<td>13800</td>
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<td>638</td>
<td>600</td>
<td>497(sh)</td>
<td>456(sh)</td>
<td>424</td>
<td>399</td>
<td>374</td>
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<tr>
<td></td>
<td>e</td>
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<td>810</td>
<td>910</td>
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<td>8700</td>
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<td>B</td>
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<td>555</td>
<td>508(sh)</td>
<td>434</td>
<td>407</td>
<td>384</td>
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<tr>
<td></td>
<td>e</td>
<td>830</td>
<td>536</td>
<td>780</td>
<td>3610</td>
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<td>19600</td>
<td>17700</td>
<td>17100</td>
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<tr>
<td>A MoCoH₂O λ&lt;sub&gt;max&lt;/sub&gt;</td>
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<td>539</td>
<td>519</td>
<td>405</td>
<td>374</td>
<td>358</td>
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<tr>
<td></td>
<td>e</td>
<td>2180</td>
<td>7500</td>
<td>7600</td>
<td>17400</td>
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<td>25300</td>
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</tr>
<tr>
<td>B</td>
<td>λ&lt;sub&gt;max&lt;/sub&gt;</td>
<td>668</td>
<td>600</td>
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<td>474</td>
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<td>412</td>
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<tr>
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<td>2140</td>
<td>1970</td>
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<td>14500</td>
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<td>A MoH₂O₂H₂O λ&lt;sub&gt;max&lt;/sub&gt;</td>
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<td>14500</td>
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<td>22100</td>
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<tr>
<td>B</td>
<td>λ&lt;sub&gt;max&lt;/sub&gt;</td>
<td>594</td>
<td>547</td>
<td>503</td>
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<td>404</td>
<td>381</td>
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</tr>
<tr>
<td></td>
<td>e</td>
<td>1050</td>
<td>1880</td>
<td>18800</td>
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<td>26100</td>
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<tr>
<td>B</td>
<td>λ&lt;sub&gt;max&lt;/sub&gt;</td>
<td>550(sh)</td>
<td>530(sh)</td>
<td>403</td>
<td>380</td>
<td>361</td>
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<td>18600</td>
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<td></td>
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</tbody>
</table>

EtOH

|        | Di-tert-λ<sub>max</sub> | e  | 263 |
|        | max | 354 | 295(sh) | 284(sh) | 273  | 263 |
| butyl  | 23900 | 21100 | 26000 | 27700 | 27900 |     |
| MoH₂   | 1540 | 1340 | 12400 | 11600 | 11800 |     |

A = Pyridine solution ;  B = 1-Chloronaphthalene solution ;
peak positions in nanometers.
Guanazole and l-imino-5-oxoisoindoline.

Guanazole (0.99 g.) and l-imino-5-oxoisoindoline (1.46 g., 1.0 mol) were heated in boiling 2-methoxyethanol (15 c.c.) for 1.5 hrs. After 30 minutes a bright yellow solid began separating and continued to separate out over 1 hr., with ammonia evolution. Filtration and washing, drying gave a yellow powdery solid (1.93 g.). Recrystallisation from dioxan : nitrobenzene gave a microcrystalline yellow solid, m.p. 340-342° with considerable shrinkage prior to melting, turning brown above 220°. Ultra violet (DMF) $\lambda_{\text{max}}$ 258 nm (10,000).

Principal $\nu_{\text{max}}$ (Nujol) 3300, 3190, 1740s, 1650s, 1610s, 1500, 1300s, 1180, 1090, 1070, 1045, 1030, 850, 770s, 705s. Molecular ion m/e 228. Found : C, 53.51 ; H, 3.71.

C_{10}H_{8}N_{6}O requires C, 52.63 ; H, 3.53%.

M, 228.2

1-Phenylguanazole and l-imino-5-oxoisoindoline.

1-Phenylguanazole (1.75 g.) and l-imino-5-oxoisoindoline (1.64 g.) were dissolved in 2-methoxyethanol (20 c.c.), with stirring under nitrogen. After 2.5 hrs., heating under reflux conditions, during which time ammonia was evolved, the initially clear yellow solution began precipitating a bright yellow solid. After 4 hrs., (when ammonia evolution had slackened), the reaction mixture was cooled and allowed to stand at room temperature overnight. The solidified mass was filtered off and washed with ether giving a pale yellow crystalline solid (1.41 g.). Evaporation of the filtrate and work up with chloroform gave a further quantity of solid as a brown crystalline mass (1.68 g.). Fractionation of the initial yellow crystals using a mixture of ethanol and n-butanol gave an insoluble product A (0.50 g.) pale yellow, and a soluble product B, crystallising
from cold solution as lemon yellow crystals (0.73g.). Both fractions were subsequently purified by recrystallisation from chlorobenzene, washing with alcohol and drying to give,

**Fraction A** (0.39g.), pale yellow crystals, m.p. 297-299°

mol. ion from mass spec. 433. UV (chlorobenzene) \( \lambda_{\text{max}} \) 298 nm (14,600), 350nm (24,600).

Principal \( \nu_{\text{max}} \) (Nujol) 3360s, 3320s, 1755s, 1660s, 1600, 1510s, 1440s, 1355, 1315, 1295, 1180, 1170, 1145, 1095, 1075, 1035s, 780, 770s, 710s, 690, 685 cm\(^{-1}\).

Found: C, 66.32; H, 3.47; N, 22.28

C\(_{24}H_{15}N_{7}O_{2}\) requires C, 66.51; H, 3.49; N, 22.62%

**Fraction B** (0.35g.), lemon yellow crystals, m.p. 255-258° (red on melting), mol. ion from mass spec. 304. P.m.r. (DMSO)

-0.89 \( \tau \) (s) 1 proton, 1.73-2.73 \( \tau \) (m) 9 protons, 3.29 \( \tau \) (s) 2 protons. UV (chlorobenzene) \( \lambda_{\text{max}} \) 303 nm (6,200), 345nm (12,200)

Principal \( \nu_{\text{max}} \) (Nujol) 3280s, 1735s, 1665, 1650s, 1520, 1505, 1435, 1315, 1305, 1285, 1090, 1070, 1050, 915, 865, 800, 775s, 765s, 755s, 700s, 675 cm\(^{-1}\).

Found: C, 63.04; H, 4.14; N, 27.65.

C\(_{16}H_{12}N_{6}O\) requires C, 63.15; H, 3.97; N, 27.62%

The third fraction from the reaction mixture was found, by mass spectrometry, infra-red spectroscopy and elemental analysis to correspond to a mixture of the two compounds above, together with a smaller amount of higher molecular weight material.
Guanazole and 1-imino-3-phenyliminisoindoline.

Guanazole and 1-imino-3-phenyliminisoindoline were reacted in stoichiometric proportions in 2-methoxyethanol, eliminating ammonia and precipitating an orange-brown solid. The solid showed no melting point up to 320°C. Elemental and infra-red analysis showed this product to be a mixture of two unit condensation products. The isolation of the components was not achieved primarily due to the general insolubility of the products in organic solvents. UV (DMF) \( \lambda_{\text{max}} \) 353nm, 337 (sh)nm, 313 nm. Principal \( \nu_{\text{max}} \) (Nujol) 3270, 3140, 1660s, 1630s, 1560, 1415, 1310, 1275, 1165, 1100, 1040s, 865, 760s, 720, 685 cm\(^{-1}\).

Found: C, 53.97; H, 4.02; N, 41.78.

C\(_{10}\)H\(_9\)N\(_7\) requires C, 52.87; H, 4.00; N, 43.15.

C\(_{10}\)H\(_9\)N\(_6\) requires C, 52.63; H, 3.53; N, 36.83%.

1-Phenylguanazole and 1-imino-3-phenyliminisoindoline.

1-Phenylguanazole (1.75g.) and 1-imino-3-phenyliminisoindol-ine (2.21g.) were heated in 2-methoxyethanol for 5.5 hrs. During the heating period ammonia was evolved and a solid formed. Cooling and filtration gave a yellow-brown powder (0.66g.). The addition of excess ether to the filtrate gave a quantity of yellow solid (0.42g.). A chromatographic separation of the first fraction, on an alumina column using chloroform as eluent, gave a main component which was isolated as an orange-brown microcrystalline powder, m.p. 135-140°C. UV(EtOH) \( \lambda_{\text{max}} \) 228nm (32,300), 304 nm (11,200), 356 nm (16,500).

Principal \( \nu_{\text{max}} \) (Nujol) 3330, 3060w, 1640s, 1595, 1565, 1510s, 1435, 1310s, 1220, 1190, 1095, 1080, 1045, 1035, 1015, 910, 870, 840, 775, 760s, 755, 690 cm\(^{-1}\).
The fraction recovered from the original filtrate was recrystallised several times from n-butanol to give a yellow-brown solid, m.p. 198-202°. UV (EtOH) λ max 228nm (31,200), 260 nm (20,000), 312 nm (9,800), 351 (13,500). Molecular ion m/e 379.

Principal λ max (Nujol) 3470w, 3320, 3220, 3050w, 1660s, 1635s, 1595s, 1560, 1530, 1505, 1310s, 1225, 1190, 1170, 1095, 1045s, 1015, 915, 870, 775s, 760s, 695s, 675 cm⁻¹.

l-Phenylguanazole and benzaldehyde.

(a) l-Phenylguanazole (1.08g.) was heated with benzaldehyde (4c.c.) under a nitrogen atmosphere. All the solid material dissolved on warming and began separating out at 90°. At 140-150° the solid redissolved to give a clear red solution. The reaction was taken to 160-170° for a few minutes. Cooling and standing overnight gave no solid products. Heating to 160-170° with an equivalent volume of nitrobenzene and cooling gave a pale yellow crystalline solid which was isolated washed thoroughly with ether and dried (1.1g.), m.p. 132-133°. Molecular ion m/e 351. Yield 55%. P.m.r. (CDCl₃), 0.56τ(s), 0.59τ(s), 2 protons, 1.95 τ(m) 6 protons, 2.50 τ(m) 9 protons. UV (MeOH) λ max 279nm (22,600), 355 (sh) nm (11,000).

Principal λ max (Nujol) 3090w, 1610s, 1600, 1570s, 1500s, 1410, 1345s, 1310, 1210, 1145s, 1055, 990, 915, 775, 760s, 740, 685s cm⁻¹.
(b) 1-Phenylguanazole (1.0g.) and benzaldehyde (4c.c.) were heated to 85-95° on a steam bath, under a nitrogen atmosphere, for 1 hr. The yellow-orange solid formed was filtered off and washed with ether to give a cream coloured crystalline solid (1.33g.), m.p. 233-236°. Recrystallisation from ethanol gave glistening cream plates, m.p. 234-236°. Yield 89%. Molecular ion m/e 263. UV (EtOH)λ max 269 nm (13,100), 322 nm (10,400). P.m.r. (DMSO) 0.92 τ(s), 0.96 τ(s), 0.97 τ(s), 1 proton, 1.9-2.7 τ(m) 10 protons, 3.45 τ(s) 2 protons.

Principal V max (Nujol) 3370, 3330, 3140s, 1650s, 1610, 1595, 1565, 1520s, 1440, 1350, 1290, 1215, 1120, 1075, 985, 915, 765s, 695s cm⁻¹.

Guanazole and benzaldehyde.

Guanazole (1.0g.) and benzaldehyde (5c.c.) were heated to 160-170° as above. At ca 110° a solid separated out and redissolved on further heating, and again a solid came out of solution at ca 150°. The cooled mixture was filtered and the solid product washed and dried with ether, (2.22g.), m.p.214-217°. Recrystallisation from chlorobenzene gave small yellow needles, m.p. 216-218°. Yield 80%. Molecular ion m/e 275. UV (chlorobenzene)λ max 350 nm (8000).

Principal V max (Nujol) 3260, 3130, 1595s, 1585s, 1500, 1355, 1340, 1310, 1240, 1215, 1200, 1150, 1125s, 1045, 1030, 990, 940, 880, 860s, 795, 765s, 725s, 690s cm⁻¹.
Guanazole and anisaldehyde (para-methoxybenzaldehyde).

Guanazole (1.0g.) and anisaldehyde (8c.c.) were heated to 160-170° for 1 hr., cooled, and the mixture worked up with ether giving a yellow solid (1.34g.), m.p. 240-243°. Yield 62%. Recrystallisation from n-butanol gave the material as a pale yellow powder, with an unchanged melting point. P.m.r. (DMSO) -1.95 τ(b,s) 1 proton, 1.04 τ(s) 1 proton, 2.10 τ(d) 2 protons and 2.95 τ(d) 2 protons—corresponding to an A<sub>2</sub>B<sub>2</sub> system with J<sub>AB</sub> ≈ 9 cps, 4.00 τ(b,s) 2 protons.

UV (EtOH) λ<sub>max</sub> 223 nm (6,900), 230 (sh) nm (6,100), 286 (sh) nm (7,800), 294 (sh) nm (8,800), 322 nm (10,400).

Principal λ<sub>max</sub> (Nujol) 3330, 3130, 1660s, 1600s, 1575s, 1520s, 1450, 1350, 1315, 1260s, 1225, 1165s, 1115, 1080, 1035, 990, 900, 835s, 765s, 720 cm<sup>-1</sup>.

1-Phenylguanazole and anisaldehyde.

1-Phenylguanazole (1.0g.) and anisaldehyde (8c.c.) were heated as above to 160-170° for 1 hr. Cooling and filtration of the mixture gave a bright yellow powder (1.85g). Recrystallisation from n-butanol gave a yellow microcrystalline solid, m.p. 155-160°. Yield 80%. P.m.r. (DMSO) 0.75 τ(s) 1 proton, 0.81 τ(s) 1 proton, 1.70-2.95 τ(m) 13 protons. UV (n-butanol) λ<sub>max</sub> 298 (sh) nm (25,200), 322 nm (32,200), 352 (sh) nm (27,300).
Principal $\nu_{\text{max}}$ (Nujol) 1605 s, 1580, 1525 s, 1430, 1350, 1320 s, 1275 s,
1260, 1225, 1160 s, 1035, 1020, 835 s, 760, 690 cm$^{-1}$.

Found: C, 69.91; H, 5.24; N, 17.18.

C$_{24}$H$_{21}$N$_2$O$_2$ requires C, 70.06; H, 5.14; N, 17.02%.

1-Imino-3-oxoisooindoline and 2,5-diamino-3,4-dicyanothiophene in 2-methoxyethanol.

A mixture of 2,5-diamino-3,4-dicyanothiophene (3.28 g.) and 1-imino-3-oxoisooindoline (2.92 g., 1.0 mol) was heated in boiling 2-methoxyethanol for 16.5 hrs., the mixture evolving ammonia during the process. The solid material from the cooled reaction mixture was filtered off and washed with dry ether, giving a tan coloured solid (5.7 g.), identified by mass spectrometry (m/e 293 as molecular ion) and infra-red spectroscopy as 1-(5-amino-3,4-dicyano-2-thienyl)imino-3-oxoisooindoline. The addition of an excess of ether to the filtrate gave a bright yellow solid. A thin layer chromatogram of this material, on alumina using chloroform as the mobile phase, showed three main constituents, a main component yellow RF 0.69 and two minor components yellow-orange in colour RF 0.48 and 0.28. A preparative t.l.c. run using alumina plates and chloroform gave, on extraction with chloroform, the major fraction RF 0.69, (0.33 g.), m.p. 197°. Mass spectrometry gave a molecular ion of m/e 703.

Principal $\nu_{\text{max}}$ (Nujol) 3420, 3270, 3050, 1740 s, 1720 s, 1645 s, 1620,
1600, 1540s, 1505s, 1290s, 1260s, 1200, 1185, 1125s, 1090s, 1075, 1040, 965, 880, 775, 765, 735s, 710s, 690 cm$^{-1}$.

Found : C, 61.23 ; H, 3.83 ; N, 14.12 ; S, 4.02.

C$_{36}$H$_{29}$N$_5$O$_7$S requires C, 61.44 ; H, 4.15 ; N, 13.93 ; S, 4.57% M, 703

1-Imino-3-oxoisoindoline and 2,5-diamino-3,4-dicyanothiophene in 2-ethoxyethanol.

A mixture of oxoisoindoline (1.46g.) and 2,5-diamino-3,4-dicyanothiophene (1.64g.) in 2-ethoxyethanol (15c.c., distilled b.p.134-135°) was heated under reflux for 11 hrs. During the heating period ammonia was evolved and a brown solid deposited. Cooling overnight and filtration gave the yellow-brown solid. Excess ether on the filtrate gave more yellow solid. The combined fractions (1.5g.) were taken up in boiling methanol giving an insoluble fraction (0.61 g.) and a soluble fraction crystallising on cooling (0.40g.). A quantity of the soluble fraction was chromatographed on alumina using chloroform as mobile phase. Two main bands were observed, a main component RP 0.73 (yellow), a minor component RP 0.56 (yellow), as well as a non-mobile material. On a preparative experiment a sample of this methanol soluble fraction (0.25g.) gave, on extraction with chloroform and isolation, the more mobile component as a bright yellow solid (0.15g.), m.p. 172°. Mass spectrometry gave a molecular ion of m/e 731.

Principal $\nu_{max}$ (Nujol) 3410, 3280, 3050, 1735s, 1715s, 1645s, 1615s, 1535s, 1505, 1290s, 1260s, 1180, 1125s, 1090, 1075, 1035, 965s, 885, 860, 775, 760, 735s, 710s, 690 cm$^{-1}$.

Found : C, 62.22 ; H, 4.69 ; N, 13.57 ; S, 4.28

C$_{38}$H$_{23}$N$_5$O$_7$S requires C, 62.37 ; H, 4.55 ; N, 13.40 ; S, 4.38%. M, 731.8
**2,5-Diamino-3,4-dicyanothiophene and anhydrous ammonia**

A saturated solution of the thiophene compound (2.3g.) in 2-methoxyethanol (10c.c.) was heated to 100-110° for 5 hrs., in a sealed tube, with anhydrous ammonia (25c.c.). On cooling excess ammonia was vented off and the residual solution worked up with ether giving an orange-brown solid. This solid was dissolved in methanol (a small amount of undissolved material being filtered off) and chromatographed on alumina. The main component consisted of a mobile yellow band, eluted with methanol. Slow evaporation of the eluate gave a yellow-brown crystalline product, (0.44g.), decomposing slowly above 270°, but showing no melting point up to 330°.

P.m.r. (DMSO) -2.0 τ(b,s), 3.28 τ(s) in ratio 1:2.7.

Principal νmax (Nujol) 3440s, 3330s, 2250, 2225s, 1650s, 1595s, 1500s, 1370, 1235, 1185s, 1100, 865 cm⁻¹.

Found : C, 44.36; H, 2.00; N, 34.21; S, 19.81.

(C₆H₄N₄S)ₙ requires C, 43.89; H, 2.46; N, 34.13; S, 19.53%. 

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**Note:** The provided text is a transcription of the content visible in the image.
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