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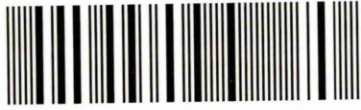
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**Novel Oligomeric and Polymeric Materials based upon the
Dibenzotetraaza[14]annulenes**

Nicholas Ian Challoner, BSc(Hons) CChem MRSC

**A thesis submitted to Sheffield Hallam University in partial fulfilment of the
requirements for the degree of Doctor of Philosophy**

July 2000



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Abstract

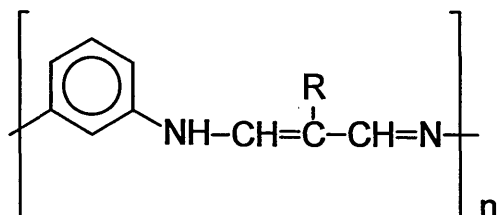
The class of compounds known as the dibenzotetraaza[14]annulenes have been of particular interest over the past 25 years, with the initial impetus for research being the relationship they hold with the naturally occurring porphyrins.

The main aim of the work undertaken was to establish the potential of dibenzotetraaza[14]annulene type systems for the development of novel materials whose applicable behaviour was likely to fall into one of the following three categories; liquid crystals, organic conductors, and chelating systems. Additionally the chemistry involved with the synthesis of these types of materials was interesting in its own right and provided a platform for the author to increase his own knowledge of chemistry.

The research undertaken may be broadly classified into the following areas : 1. The preparation of linear Schiff base polymers, 2. The preparation of dibenzotetraaza[14]annulenes (metal complexes and free ligands), 3. The preparation of 1-D and 2-D unsymmetrical macrocyclic complexes, and 4. The preparation of polymeric materials incorporating dibenzotetraaza[14]annulenes both as part of the polymeric backbone and as pendant side chains in a comb type polymer.

1. The preparation of linear Schiff base polymers

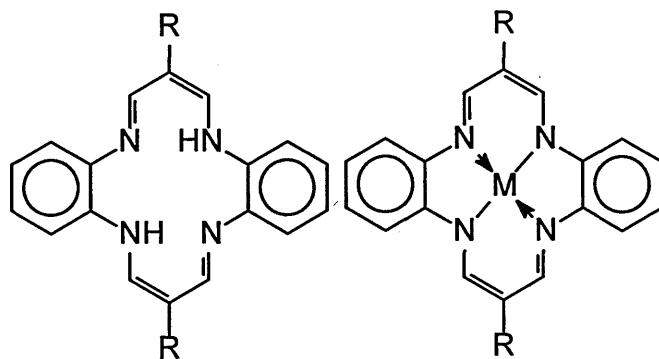
The Schiff base condensation of phenylenediamines with malondialdehydes has enabled the preparation of materials of the type illustrated below.



Examination of the materials by differential scanning calorimetry has shown that many of the materials exhibit interesting thermal transitions from one crystalline state to another. However the use of thermal microscopy has not shown any of these phases to be liquid crystalline transitions.

2. The preparation of dibenzotetraaza[14]annulenes (metal complexes and free ligands)

An extensive array of dibenzotetraaza[14]annulenes have been prepared, generally by a one step process involving the reaction of ortho-phenylenediamine and various 2-substituted malondialdehydes in the presence of a suitable acid catalyst and solvent.

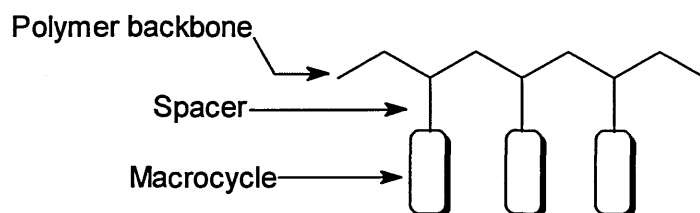


3. The preparation of 1-D and 2-D unsymmetrical macrocyclic complexes

The introduction of unsymmetricality into the dibenzotetraaza[14]annulenes has been of interest since dipole-dipole interactions between molecules may lead to enhanced crystalline stacking, which in turn has a direct effect on any liquid crystalline or semiconducting properties the material may exhibit. Consequently the preparation of unsymmetrical dibenzotetraaza[14]annulenes has been undertaken, which has often required extended stepwise synthetic reaction pathways involving the use of protecting reagents. Small quantities of pure materials have been prepared and are believed to be the first of their type.

4. The preparation of polymeric dibenzotetraaza[14]annulenes

The incorporation of dibenzotetraaza[14]annulenes into a polymeric system has been examined in two ways. The initial study concentrated on the incorporation of the macrocycle directly into the polymer backbone and involved the reaction of suitably functionalised dibenzotetraaza[14]annulenes with linking groups such as para-phenylenediamine. The additional study has focussed on a method of forming polymers which include the macrocyclic complexes as pendant side chains in a comb type polymeric arrangement (illustrated below).



At present the preparation of a polymer of this type has not been achieved. However an extensive study into the attachment of groups to the macrocycles which are capable of undergoing polymerisation has been undertaken which has established the potential use of the Gabriel synthesis of amines and the Wittig reaction as potential methods of attachment.

Chapter 1

General Introduction

The class of compounds known as the dibenzotetraaza[14]annulenes has been of particular interest over the last 25 years, with the initial impetus for research being the relationship that they hold with the naturally occurring porphyrins^{1,2} and metalloporphyrins^{3,4}.

The main aim of the work reported here is an investigation into the potential of dibenzotetraaza[14]annulene type systems for the development of novel materials (particularly polymeric materials) whose applicable behaviour is likely to fall into one of three categories; liquid crystals, organic conductors, and chelating systems.

In terms of general structural parameters the dibenzotetraaza[14]annulene ring system (Fig. 1) is formally a cyclic dimer (Fig. 2, $x=2$), whose corresponding cyclic monomer is a diazepine (Fig. 3) and whose repeating polymer unit is that shown in Fig. 2.

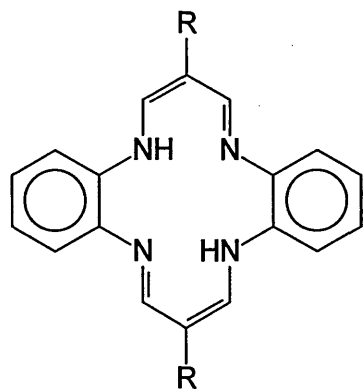


Fig. 1 Dibenzotetraaza[14]annulene ring

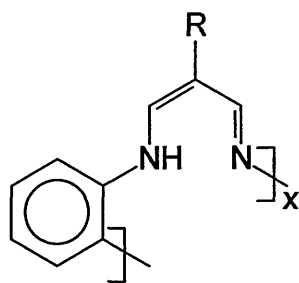


Fig. 2 Repeat unit of the DBTAA ring

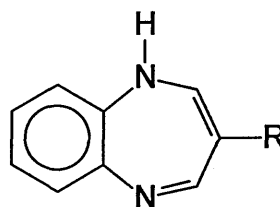


Fig. 3 Benzodiazepine

A variety of linear and branched-linear polymers can be envisaged in which features related to the repeat unit of the dibenzotetraaza[14]annulene ring system are present. Accordingly a series of synthetic objectives was identified at the start of the project. The targets included two series of main-

chain polymers. In the first series (Fig. 4) repetitive malondialdehyde bis-imines can be connected by either inflexible aryl rings (e.g. from *ortho*-, *para*- or *meta*-phenylenediamines (Fig. 4 a.) or flexible alkyl chains (Fig. 4 b.).

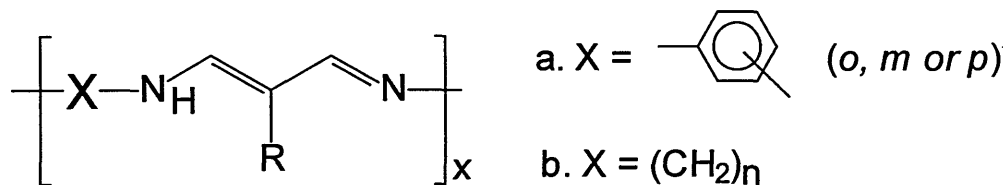


Fig. 4 Main chain polymers.

In the second series (Fig. 5) the dialdehyde imine components are provided by appropriate dibenzotetraaza[14]annulenes (e.g. Fig. 1 where R = CHO). Schiff base condensation with appropriate diamines could then provide polymer chains that include *o*-, *m*-, *p*-aryl (Fig. 5 a.), alkyl (Fig. 5 b.) or even dibenzotetraaza[14]annulene (Fig. 5 c.) components.

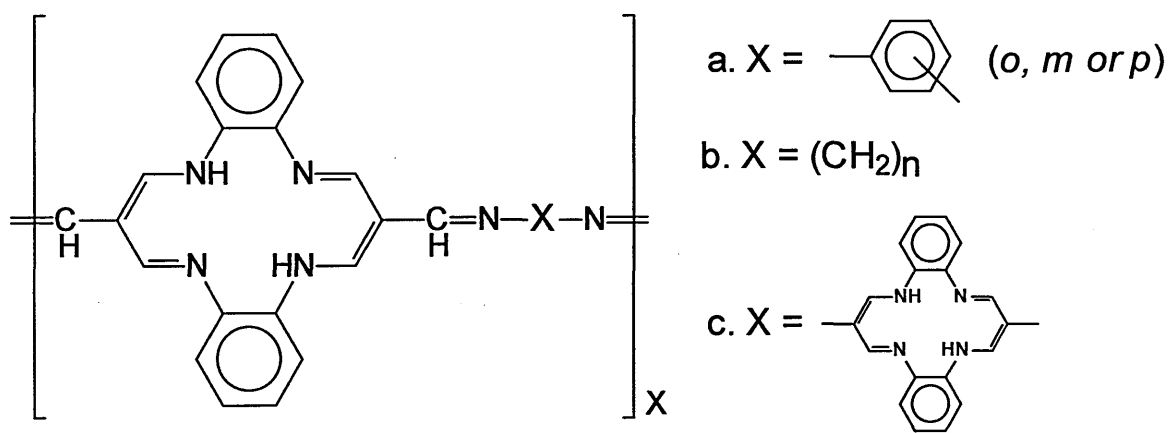


Fig. 5 Main chain polymers incorporating the dibenzotetraaza[14]annulene ring.

Alternatively a series of side-chain polymers can be envisaged where the components of interest (e.g. dibenzotetraaza[14]annulene rings) are present in each repeat unit, but as lateral substituents connected to the polymer backbone (e.g. polysiloxane) via a decoupling spacer and an appropriate linking group (x), as summarised in Fig. 6. The decoupling spacer is necessary if the

dibenzotetraaza[14]annulenes are to have any freedom to form ordered domains in materials based on polymer backbones whose preferred conformations are highly randomised.

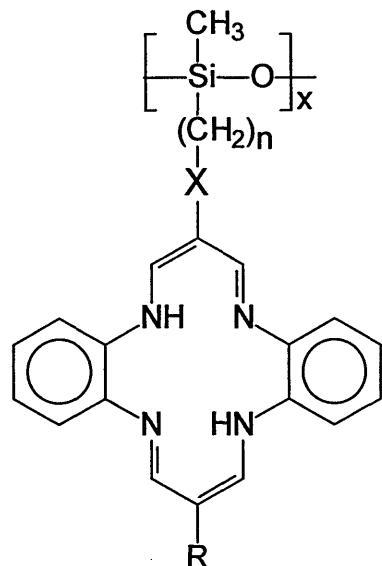


Fig. 6 Side chain polymer.

The foregoing synthetic objectives (Fig. 4-6) define a major program of work implying, as they do, precursor syntheses that involve a variety of dibenzotetraaza[14]annulenes (some entirely novel) and, therefore, a variety of the highly labile malondialdehydes. It was also hoped to undertake limited evaluation studies on at least some of the target materials. The evaluations would address potential liquid crystallinity, conductivity and chelating ability in appropriate products, where there are grounds for predicting such properties. Some known structure - property correlations for known liquid crystalline and conductive polymers are discussed later (chapters 2 and 3).

Discotic liquid crystallinity has been demonstrated in phthalocyanine materials⁵⁻¹⁰. Simple phthalocyanines tend to crystallise too well for mesophase formation to be favourable, but the inclusion of thermally mobile substituents (e.g. long alkyl chains) seems to provoke mesophase formation in stepwise melting of suitable phthalocyanine derivatives. Dibenzotetraaza[14]annulenes have not previously been evaluated in comparable ways and so, although liquid crystalline behaviour was not a particular aspiration of our molecular designs, some thermal characterisation was carried

out. Side chain polymers (Fig. 6) may be the most promising liquid crystalline targets (there is an interest in the liquid crystalline properties of side chain porphyrin and phthalocyanine polymers also¹¹), but considerable optimisation studies of the structural variables (e.g. x, n, X and R in Fig. 6) would be required to evaluate the possibilities thoroughly. The main chain polymers could also offer liquid crystallinity since both of the designs illustrated in Figs. 4 and 5 include rigid units and cyclic structures that are relevant to the generation of mesophases in several known main-chain liquid crystal polymers¹².

Some degree of electrical conductivity seems a realistic possibility for each of the three polymer types, and is already established for certain dibenzotetraaza[14]annulene derivatives (see chapter 3) albeit at very low σ values. Likely applications for such materials are certainly not related to power transmission or any other 'metallic' property. However, sensor properties of metallated dibenzotetraaza[14]annulenes are promising and the potential for fabrication into operable sensors has been shown to exist¹³⁻¹⁵. There is also the potential for the use of the polymers of interest in the areas of antistatic coatings and electromagnetic shielding.

The conduction of charge carriers (e.g. electrons) requires the formation of a conduction band by the overlap of appropriate molecular orbitals to form delocalised, supramolecular orbitals. A structural requirement of charge carriers that follows from the above, is a fully conjugated π -system in the ground state representation of the polymer (e.g. as in polyacetylene or polypyrrole). The conjugation is essential for the transmission of the charge-carrying defects, such as solitons or polarons, which are implicated in polymer conductivity. Suitable conjugation is not immediately apparent in the conventional representation given for dibenzotetraaz[14]annulenes (e.g. Fig. 5) or linear polymeric counterparts (e.g. Fig. 4). These simplified representations, however, overlook the known planarity of the Hiller type dibenzotetraaza[14]annulenes (ie. those prepared using dialdehydes) or the known bond lengths in the propanediiminato bridges². A more complete representation of these structural segments is shown in Fig. 7, where delocalisation of the π -system and sharing of the amino hydrogen (and thus the metal in metallated derivatives) implies that both nitrogens are sp^2 hybridised giving three coplanar bonds and one p-orbital extending the potential conjugation of the system. Thus

polymers of the type illustrated in Fig. 4 (although not in the zig-zag conformation shown) and Fig. 5 seem potentially conductive although careful doping may be required to optimise the electron population.

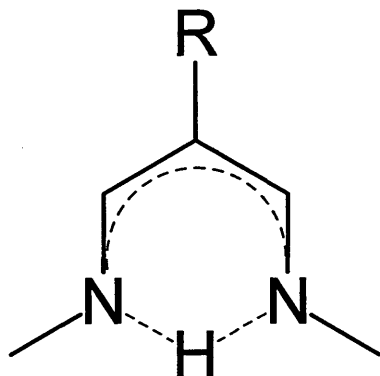


Fig. 7 Structural representation of the propanediiminato bridge of dibenzotetraaza[14]annulene.

Polymers of the type illustrated in Fig.6 are different, and offer intriguing possibilities for semiconducting dibenzotetraaza[14]annulene derivatives. Spacer manipulation in studies of side-chain liquid crystals¹⁶ has shown that in side-chain polymers with long spacers, e.g. $(\text{CH}_2)_{11}$, terminal substituents that crystallise well as small molecules also form highly crystalline domains in polymers. Since crystalline domains in ordered films of macrocyclic materials can sustain electrical conductivity, side-chain architectures based on molecules of the type illustrated in Fig. 6, but metallated and further doped , may mimic that behaviour but in polymeric materials.

The development of new macromolecular chelates is of great interest due to their thermal stability, electrical conductivity and good catalytic activity in many organic reactions¹⁷⁻¹⁹. Recent studies have involved the synthesis²⁰ and characterisation²¹ of chelating poly(vinylketone) materials.

Poly(vinylketone) is prepared by the oxidation of poly(vinylalcohol) with potassium permanganate in alkaline media ($\text{pH} > 12$). The polymer exists as a 1,3-dione and, hence, the structure facilitates the formation of chelated complexes via keto-enol tautomerism. The possible keto-enol forms are illustrated below (Fig. 8).

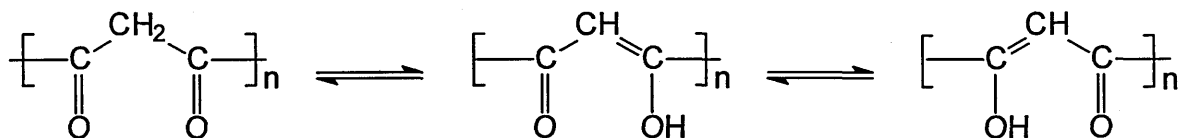


Fig. 8 Keto-enol tautomerism within poly(vinylketone).

The polymer ligand may chelate to a metal ion through one or two electron donor groups and the geometrical structure of the obtained chelates depends upon the manner of attachment. Three types of chelation may be considered-

1. The enolate anion formed by the weakly acidic enol tautomer of poly(vinylketone) may allow coordination to metal ions via the oxygen atom to form six-membered complexes²².
2. An oxygen-chelated complex may be considered that is the simple Lewis acid-base adduct, formed from the donation of electrons from the oxygen atoms of the carbonyl groups to acceptor species²³.
3. Interpolymeric complexes may be formed by chelation from bridging enolate ligands.

Coordination polymers of this type have been prepared with the metal ions Cu^{2+} , Ni^{2+} , Co^{2+} , Cd^{2+} and Hg^{2+} . The metal content in the polymers was found to be consistent with 1:2 metal:poly(vinylketone) stoichiometry. The proposed structure for the polymeric chelates is illustrated below, (Fig. 9), and involves a monobasic bidentate coordination mechanism.

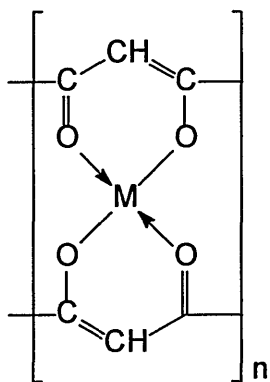


Fig. 9 Structure of the polymeric complexes of poly(vinylketone), $\text{M} = \text{Cu(II)}$, Ni(II) , Co(II) , Cd(II) , Hg(II) .

Analogies may be drawn from this work and applied to the systems that have been discussed. Metal complexes of main chain and side chain polymers may be envisaged that involve the chelation of the metal ion by the four nitrogen atoms that are situated in a plane. This type of complex has been extensively studied²⁴, and indeed the involvement of metal template effects during the formation by ring closure of tetraazamacrocycles may be important in terms of yield and the kinetics of the ring closure, as well as playing an integral part in the control of side reactions.

Chelation of metal ions by polymers of the type illustrated in Fig. 4 may result in the formation of interesting inter- and intramolecular polymeric compounds, (Fig. 10), that are clearly related to the poly(vinylketone) system. The chelating species are the nitrogen atoms that are situated within the polymer backbone. The conformation of the main-chain system is a determinant of the feasibility of this idea (cf. figs. 4 and 10).

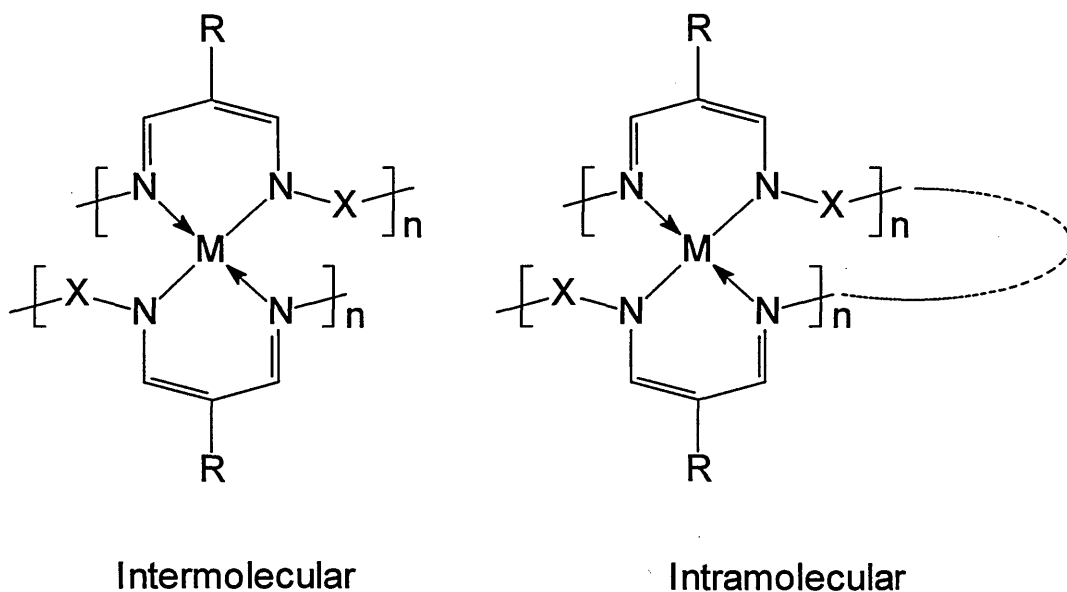


Fig. 10 Intermolecular and intramolecular polymers.

Chapter 2

Liquid Crystals

1. Introduction

The term *liquid crystal* signifies a state of molecular aggregation that exists as an intermediate between the crystalline solid and amorphous liquid states. Predominately, substances that exist in this state show a high degree of anisotropic character in many of their properties, and yet are still capable of a certain degree of fluidity. Liquid Crystalline or *mesomorphic* behaviour was first observed by Reinitzer²⁵ and Lehmann²⁶ towards the end of the last century and since then many organic compounds have been shown to exhibit liquid crystalline behaviour^{27,28}. Molecular shape is an extremely important requirement for mesomorphism to be exhibited. In order for molecular ordering to occur there must be a high geometric anisotropy, and the molecule should generally be rod shaped (i.e. long and relatively narrow) although disc shaped systems are now of interest also. The detailed molecular geometry of the liquid crystalline material has a pronounced effect on the number and type of mesophases which it may pass through before it is transformed into the isotropic liquid.

Transitions of liquid crystals from anisotropic solid through the mesomorphic state to the isotropic liquid may be brought about by two processes:

Thermotropic Mesomorphism

The transition through the liquid crystalline state is brought about by purely thermal processes.

Lyotropic Mesomorphism

The transition through the liquid crystalline state is brought about by the influence of solvents.

2. Structural classification of liquid crystals

The classification of liquid crystalline phases has given rise to a great deal of confusion. This is largely a consequence of the underlying phenomena which make liquid crystals so interesting in themselves, namely the wide variation of phase behaviours which are exhibited. However, the progress now achieved in the study of liquid crystalline materials has given us enough firm understanding of the subject to outline the basic structural classifications.

2.1 Thermotropic liquid crystals

Nomenclature²⁹ proposed for the classification of thermotropic liquid crystals broadly separates them into three types: *nematic*, *smectic* and *cholesteric*.

2.1.1 Nematic liquid crystalline phases

The nematic phase exists as a semi-isotropic liquid³⁰, which shows only short-range order in all directions. However, a long-range orientational order of the molecular long axes is exhibited by the molecules which tends to be parallel to a common axis called the director \mathbf{n} (Fig. 2.1). Thus it differs from the isotropic phase in that the molecules are spontaneously oriented with their long axes approximately parallel.

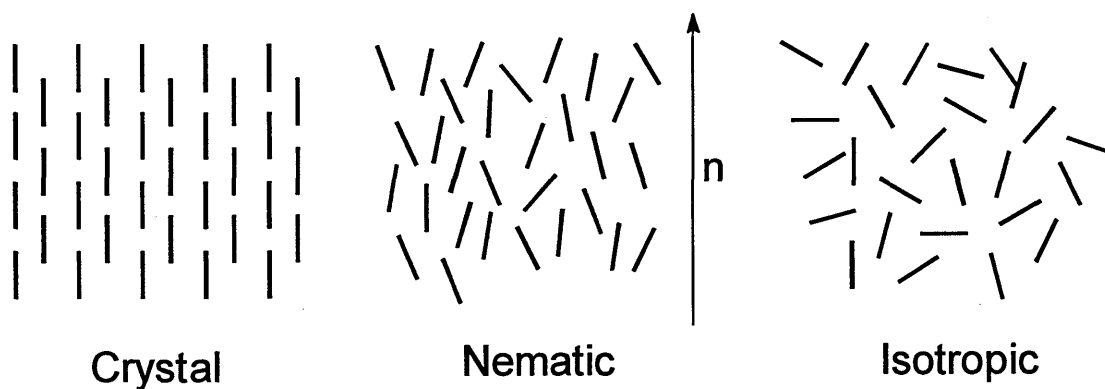


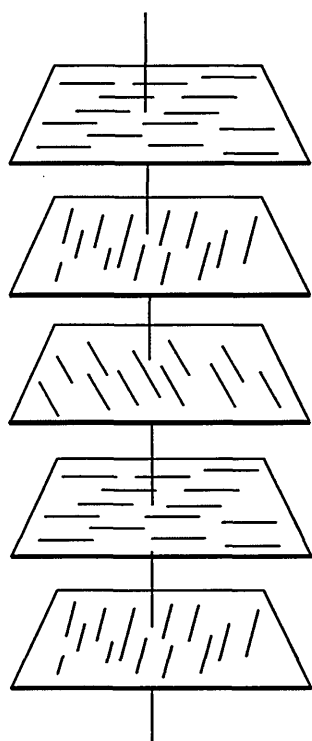
Fig. 2.1 Representation of the molecular order in the crystalline, nematic and isotropic phases.

The orientation of the director varies from point to point in the medium and studies have indicated that the composition of some nematic phases is of the order of 10^2 molecules which are called *cybotactic* groups³³, however it should be noted that in most nematics any cybotactic groups which may exist are too small to be detected by X-ray methods. In specimens where the alignment is homogenous, it is observed that optical uniaxiality is exhibited along with strong, positive birefringence. The nematic phase shows no periodicity of molecular arrangement as the centres of the molecules are distributed at random as is seen in the amorphous liquid.

The viscosity of the mesophase is relatively low (compared with other mesophases), as is shown by the high fluidity of the nematic phase, which is sometimes more fluid than the corresponding isotropic liquid formed on heating of the specimen. The fluidity of the mesophase can be attributed to the ease with which the molecules can slip by each other whilst the parallel arrangement of the mesogens is retained. In contrast, a *log-jam* effect may be considered for isotropic liquids that do not exhibit the orientational alignment found within the nematic phase. This results in a loss of fluidity.

2.1.2 Cholesteric liquid crystalline phases

As the name suggests, cholesteric liquid crystals can be observed if the molecule is a cholesterol derivative, e.g. various cholesteryl fatty acid esters. Non-sterol derivatives can also exist in a cholesteric liquid crystalline state, the only condition being a requirement for optical activity to be exhibited by the molecule; a more general phase descriptor is therefore *chiral nematic*. If a chiral molecule forms a nematic phase or if it may be incorporated into the phase in appropriate concentration, then the structure itself becomes chiral and contains a helical twist³⁰. The helical structure contained by materials which exhibit cholesteric mesophases (Fig. 2.2) possesses a screw



axis that is normal to the preferred molecular direction. The pitch of the twist results in the Bragg scattering of light and characteristic colour effects. Thermodynamically, the cholesteric phase is very similar to the true nematic as the energy of the twist forms only a minute part of the total energy associated with the parallel alignment of the molecules. An illustration of this fact often arises when a small quantity of a cholesteric substance²⁹, or a non-mesomorphic optically active substance³⁴ is added to a nematic phase, whereupon the mixture adopts a helical configuration. Unique optical properties are exhibited by cholesteric molecules due to the spiral arrangement of the molecules such as a rotatory power about a thousand times greater than that of an ordinary optically active substance.

Fig. 2.2 Schematic representation of the helical structure of cholesteric liquid crystals.

2.1.3 Smectic liquid crystalline phases

The classification of mesophases described as smectic may be further sub-classified into three groups-

- Uniaxial smectic liquid crystals with unstructured layers - *Smectic A*
- Biaxial smectic liquid crystals with tilted unstructured layers - *Smectic C*
- Smectic liquid crystals with structured layers - *Smectic B*

Smectic liquid crystals have stratified structures but a variety of molecular arrangements are possible within each stratification. Smectic A phases have an infinite fold symmetry axis perpendicular to the layers, that is to say that the molecules in each layer are upright with their centres irregularly spaced in a liquid like fashion (Fig. 2.3 i.).

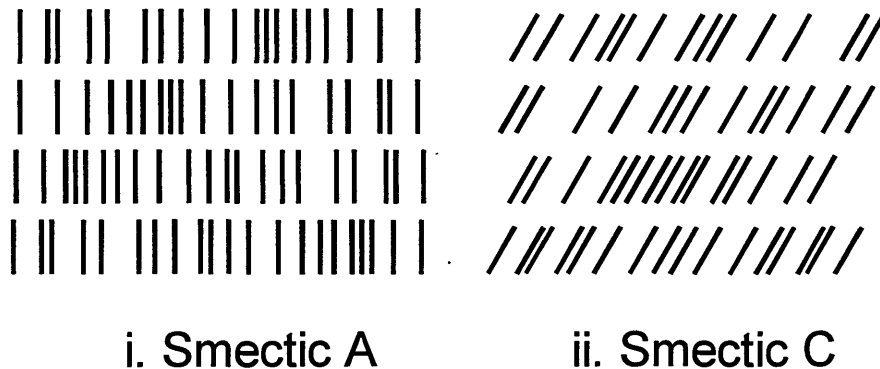


Fig. 2.3 Schematics illustrating ordering of molecules in smectic structures.

The orientational order is of the same kind as that exhibited in the nematic mesophase, but the degree of order is higher and the smectic A mesophase less temperature dependent. The thickness of the layer is of the order of the length of the free molecule. The interlayer attractions are weak in comparison with the lateral forces between molecules in the layers and as a consequence the layers are easily able to slide over one another. As we might expect the mesophase exhibits fluid properties,

although as a rule it is very much more viscous than the nematic mesophase. Often it may be the case that additional smectic phases are formed by the compound, however it is always the case that smectic A is the highest temperature smectic phase that exists. On heating, the mesophase transforms accordingly to either a nematic or cholesteric liquid crystal or into the isotropic liquid state.

Differences in the packing of the molecules accounts for the types of smectic phases which exist. The molecular centres in each layer of the smectic B phase differ from those of the smectic A phase in that they have a hexagonally close packed structure. The schematic illustration of the smectic C phase (Fig. 2.3 ii.) shows the incline of the molecules with respect to the layers i.e., the smectic C phase is a tilted form of the smectic A phase. However, differences do exist in the axial symmetry between the two phases. Since the molecules within a smectic A phase are aligned parallel to the layer normal, at thermal equilibrium the smectic A phase is optically uniaxial. This is due to the rotational symmetry exhibited about an axis parallel to the layer normal. Examination of the structure of the smectic C phase appears to indicate a uniaxial symmetry about the preferred molecular direction, this however is not the case³⁵. In the tilted structure the continuous rotational axis about the director is replaced by a twofold axis and as a result the liquid crystal phase exhibits biaxiality. In addition to the tilt there may be an ordered arrangement within the layers and the phase is accordingly labelled B_C . At least four other smectic modifications have been identified³⁶ but their structures have not yet been fully defined.

2.1.4 Discotic liquid crystalline phases

The synthesis and characterisation of the first discotic liquid crystal was carried out in the 1970's and a good understanding of the structures of the various phases exists³⁷⁻³⁹. These phases are generally formed from molecules having more or less flat aromatic cores with usually six, but sometimes four, lateral substituents, normally alkoxy or ester groups, with at least five carbon atoms (Fig. 2.4). The structures are based on the tendency of the molecular discs to align with their short axes (the normals

to the average molecular planes) parallel. The steric driving force is as clear as it is for the elongated molecules which form the phases previously examined.

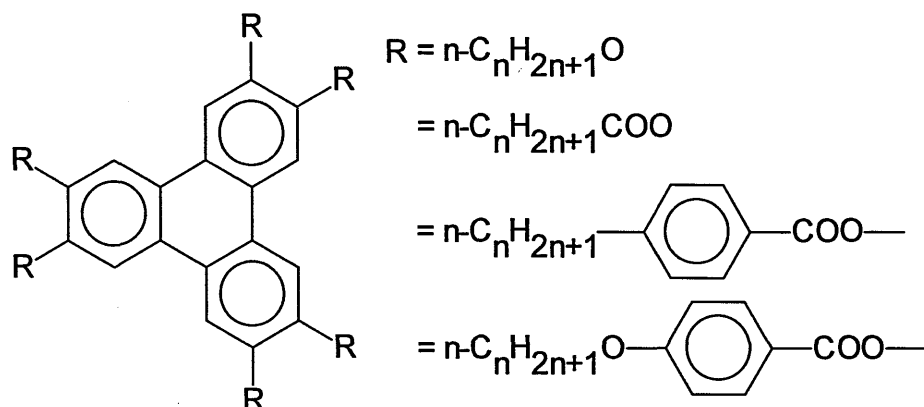


Fig. 2.4 Structure of typical discotic molecules.

The presence of the disordered side chains is crucial to the formation of discotic mesophases. The particular molecular disc-like shape determines the basic types of liquid crystal formed and is used in the nomenclature that describes the phases. These are of two types : nematic and columnar.

Discotic nematics (N_D) are anisotropic fluids which show phases that exhibit a single order parameter associated with the tendency of the discs to align parallel. The disc normals thus tend to point along a common direction thus giving rise to a director \mathbf{n} (Fig. 2.5). Re-entrant behaviour has also been observed in discotic materials⁴⁰, with an N_D phase appearing, with change of temperature, both above and below a columnar phase. The difference in the two N phases is not clear, but may be connected with molecular association as for rod-like re-entrant behaviour.

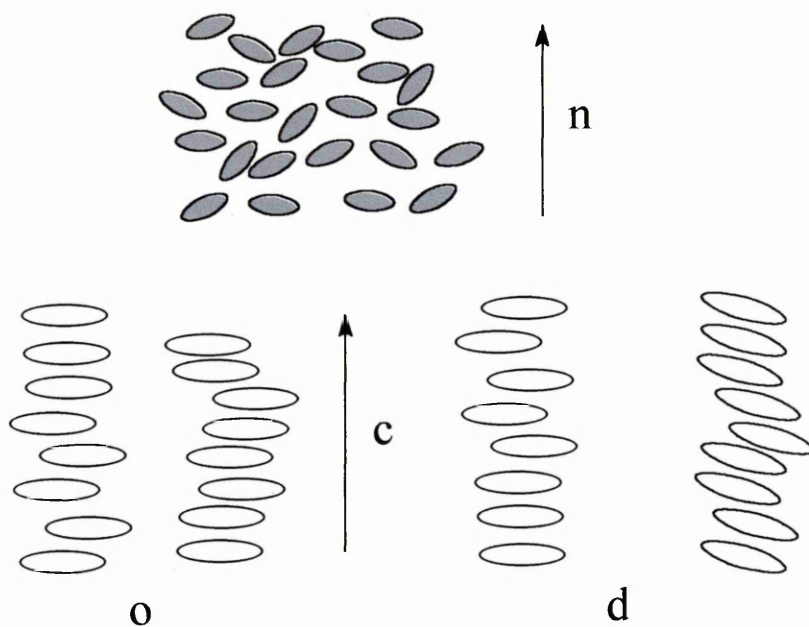


Fig. 2.5 Illustration of the structure of discotic mesophases.

Columnar phases are characterised by stacked columns of molecules, the columns being stacked together to form a two-dimensional crystalline array. Within the columns, the molecular positions may have short or long range order, but the columns are not in register along their axes, and as such these phases are not three-dimensionally crystalline.

All of the phases currently known can be characterised by the order (o) or disorder (d) of the molecular stacking in the orbitals (Fig. 2.5) and by the two-dimensional lattice symmetry of the columnar packing.

Finally, it should be noted that chiral versions of these phases also exist^{40,41}, the N_D phase being clearly analogous to the conventional cholesteric phase.

2.2 Lyotropic liquid crystals

Lyotropic liquid crystals are formed from compounds that possess amphiphilic properties (i.e. the molecule possesses a polar head group attached to one or more long hydrocarbon chains) in the

presence of suitable solvents at appropriate concentrations. At certain concentrations of the amphiphile in the solvent, between the pure amphiphile and the isotropic solution of the amphiphile in an excess of solvent, there may exist ordered arrangements of both amphiphile and solvent. These structured phases are known as micelles, and they exhibit the anisotropic characteristics of liquid crystal phases.

Examples of lyotropic liquid crystals are those produced from the dissolution of soaps and other detergents in water. As the concentration of the detergent is increased the system passes through a series of mesophases, which can be explained by the molecular packing that is exhibited by the mesogens.

The ordering of the mesogens is generally due to the environmental distribution of charge that exists within each molecule which leads to either an alignment of the molecular chains or to the occurrence of aggregation of the mesogens. The simplest lyotropic liquid crystal is created by the molecules aligning and forming layers with water sandwiched between them, and it is therefore known as the *lamellar* or *neat* phase (Fig. 2.6).

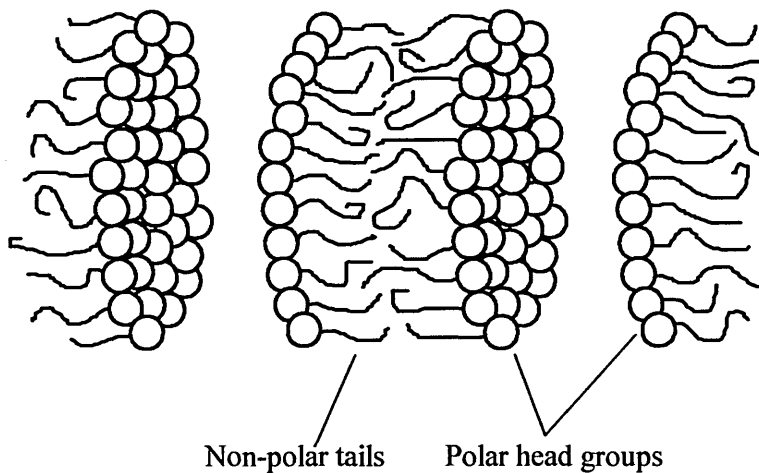


Fig. 2.6 The lamellar liquid crystalline phase.

The lyotropic nature of the hydrocarbon tails causes them to come together in a disordered and hence liquid-like fashion, resulting in a layer with the hydrophilic polar end groups at the surface which are able to sandwich the water molecules.

It is possible for these types of molecules to aggregate in another form where spherical micelles are constructed, the polar heads providing the surface of the sphere and the hydrocarbon chains filling the inside; this is known as the *cubic* or *viscous isotropic* phase. The spherical units form a body-centred cubic arrangement⁴² which has water in the space between the units. It is possible to imagine that the layers observed in the lamellar phase could indeed roll up to form cylinders. This is actually observed in the *hexagonal* or *middle* phase. The cylindrical units are arranged in a hexagonal array with all units parallel to each other (Fig. 2.7).

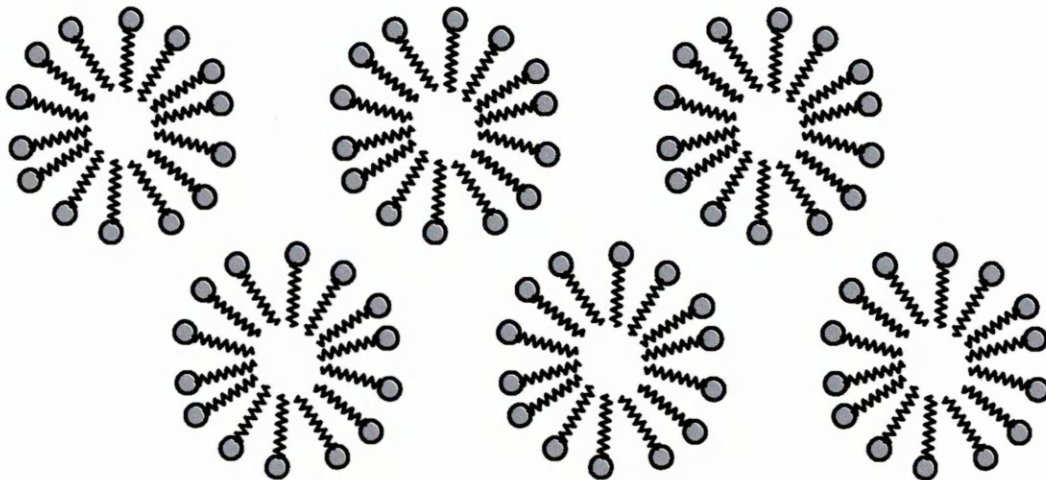


Fig 2.7 The hexagonal liquid crystalline phase

In systems where the hydrophobic compositions dominate, for example the OT-water system⁴³, then inversion of the molecules can occur resulting in inverted middle and inverted viscous isotropic phases in which the tails point outward towards the hydrophobic medium while water is trapped inside the micelle, associated with the polar head groups.

The abundance of lyotropic liquid crystals is truly amazing and extensive, particularly in living organisms⁴⁴. The structure of these *bioliquid crystals* are extremely complex and elucidation of their structures extremely difficult.

2.3 Textures of liquid crystalline phases

Deformation of the liquid crystalline phase is extremely easy, in fact distortion of the liquid crystalline structure can be caused, for example, by a dust particle. As a result, the interference patterns observed, when the liquid crystal phase is examined under a microscope between crossed polarised filters, are not the ordered interference patterns that may be expected from a superficial look at the structures but are more complex optical patterns. These textures are extremely useful in the identification of mesophases as the birefringent interference patterns observed are characteristic of the mesophases themselves⁴⁵.

3 Polymorphism - multiple mesophases in thermotropic liquid crystals

It can be common for a liquid crystal to exhibit more than one type of mesophase upon transition between the ordered solid and the isotropic liquid state. The occurrence of these multiple mesophases is known as *polymorphism*. The order of stability of the mesophases can be predicted on a scale of increasing temperature by consideration of the fact that progressive destruction of molecular order results when the temperature of any material is raised. Therefore, the higher ordered mesophases exist at temperatures closer to the solid phase. From the types of order previously described in section 1.2.1, it can be concluded that for a material which exhibits nematic and smectic mesophases the order of stability with increasing temperature would be-

Solid→Smectic B→Smectic C→Smectic A→Nematic→Isotropic

This order of stability is in complete agreement with experimentally obtained results from thermal microscopy.

The transitions which occur may be *enantiotropic*, i.e., they take place reversibly on both heating and cooling (although transition to the anisotropic solid phase is often exhibited by supercooling) or *monotropic* where the mesophase is only observed on either heating or as is more usual, cooling of the sample. An example of a polymorphic liquid crystal is shown below (Fig. 3.1).

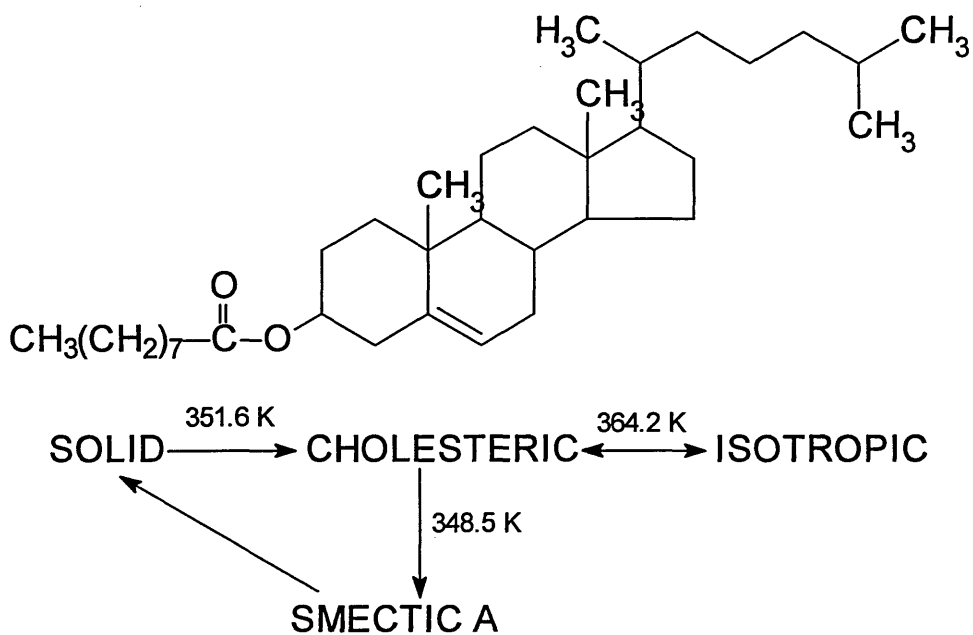


Fig. 3.1 An illustration of Cholesteryl myristate⁴⁶ and the monotropic and enantiotropic mesophases exhibited.

4 Liquid crystalline behaviour in relation to molecular structure

Consideration of molecular structure does not allow the prediction of the formation of liquid crystalline mesophases with any certainty. However, the presence of common structural features in the vast majority of thermotropic liquid crystal mesogens allows certain generalisations to be made concerning the types of molecules which are likely to exhibit liquid crystalline behaviour. The two structural features which appear to be essential to the occurrence of calamitic liquid crystalline behaviour are-

- The constituent molecules must be elongated.
- The constituent molecules must be rigid.

It should be noted however that these are only generalisations and exceptions do exist.

One group of structurally related compounds that often form liquid crystals are the substituted cholesterols of which cholesteryl myristate (Fig.3.1) is an example. From a structural examination of these molecules it is evident that this series of molecules are elongated with the interconnected rings providing rigidity, thus both criteria previously mentioned are satisfied.

4.1 Microstructural aspects of the liquid crystal core - terminal, linking and lateral groups

All liquid crystalline mesogens (excluding plastic crystals and discotic materials) have a characteristic geometric molecular shape which gives rise to anisotropic intermolecular forces with the interactions between the termini of the molecules being weaker than the lateral associations. The structure of a typical aromatic liquid crystal is shown below (Fig. 4.1) where A, B, C and D are the terminal, linking and lateral substituents of the molecule. It can be shown that in general, any structural feature such as increased core length (e.g. changing n from 1 to 2), terminal groups (A or C) which gives rigidity to an almost linear molecule should be conducive to liquid crystal formation. Even the presence of small lateral groups (D) may be tolerated and indeed used to manipulate the detailed mesophase behaviour.

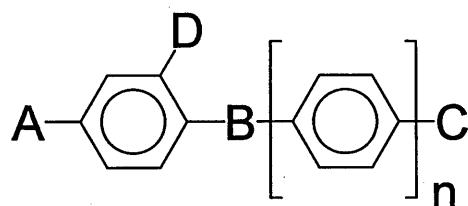


Fig. 4.1 Structure of a typical aromatic liquid crystal.

The presence of larger lateral groups leads to a decrease in the longitudinal interactions of the molecules and hence results in a reduction of the thermal stability of the mesophase. Conversely, terminal groups (A or C) which extend the molecule along its axis without increasing its breadth tend to increase the thermal stability of the mesophase.

The geometrical shape of the mesogen has a pronounced effect on the occurrence of mesophases. The introduction of kinks into the molecule, along the axis, decreases the transition temperatures of the mesophases. However, the extent to which the mesogen can be bent and still exhibit liquid crystallinity is limited since ordering of the mesogens is hindered at a certain degree from the original linear liquid crystal, and mesophase formation is suppressed (Fig. 4.2).


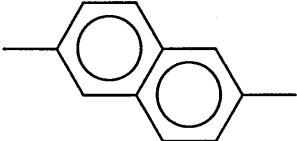
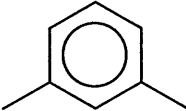
Mesogen	Mesophase
	Yes
	Yes
	No

Fig. 4.2 Effect of geometric shape on mesophase stability.

4.2 Aromatic liquid crystals

Aromatic liquid crystals form the largest group of compounds known to exhibit mesomorphism. In accordance with the rules governing mesomorphism stated previously, it was proposed⁴⁷ that for an aromatic molecule to exhibit mesomorphism it should possess the following structure-

- The molecules should be geometrically anisotropic and either rod-shaped or flat.
- There should be no more than one group in the molecule that contains a high dipole.
- The molecules should contain moderately active groups (in terms of their effect on the anisotropy of molecular polarisability, $\Delta\alpha$) such as $-\text{CCl}$, $-\text{COC}-$, $-\text{CH}=\text{N}-$, and $-\text{OCO}_2-$ towards the extremities of the molecule.

These structural requirements are considered to be the basic requirements for the formation of mesophases. The basic structure of aromatic type liquid crystals can be represented by the diagram shown below (Fig. 4.3).

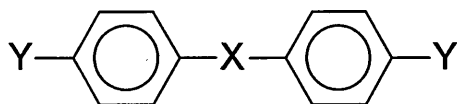


Fig. 4.3 General structure of aromatic liquid crystals.

Many of these molecules exhibit nematic, smectic and, if optically active, chiral nematic mesophases.

It is apparent even from this crude representation that the requirement of elongated molecules is satisfied by this structure. The need for rigidity is satisfied by the restriction of the linkage groups to those containing π character.

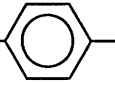
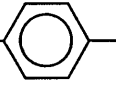
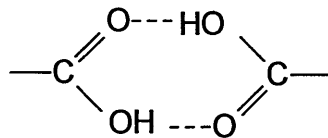
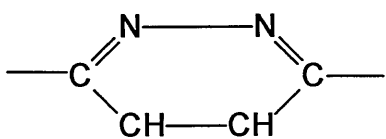
Figs. 4.4 and 4.5 show a series of molecules in which the structure of the linkage groups and end groups are listed.



X = Central Group

Type

Symmetrical Molecules

—	Biphenyl
—CH=CH—	<i>trans</i> -Diphenylethylene
—C≡C—	Diphenylacetylene
—N=N—	<i>trans</i> -Azobenzene
—CH=CH—CH=CH—	Diphenylbutadiene
—CH=N—  —  —N=CH—	Dibenzaldehydephenyldiamine
	Carboxylic Acids (Double Molecule)
	Diphenylpyridazine

Unsymmetrical Molecules

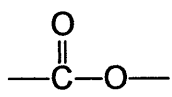
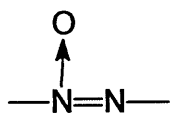
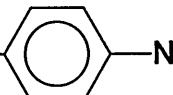
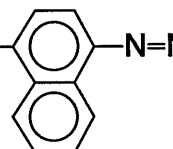
—CH=N—	Benzalaniline
	Phenyl ester of benzoic acid
	Azoxy benzene
—CH=N—  —N=N—	Benzal-p-aminoazobenzene
—CH=N—  —N=N—	Benzal-1-aminonaphthalene-4-azobenzene

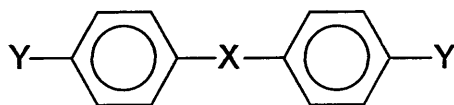
Fig. 4.4 The composition of the central group in some of the aromatic type molecules that exhibit a mesomorphic state.

The forces responsible for the formation of a liquid crystalline mesophase are primarily due to the permanent and induced dipole - dipole interactions between the individual molecules. These electronic interactions are associated with the molecular structure since, unlike in the crystalline solid, the molecules in the mesophase or *melt* are free to rotate. If the mesophase is to exist at temperatures surpassing those that have already exceeded the lattice energy of the crystal, then intermolecular polar attractions are required. Examples of terminal groups are listed below (Fig. 4.5). These may be used to illustrate the relative efficiency of various structures to stabilise a mesophase with respect to the mesomorphic thermal stability. This may be defined as the maximum temperature at which liquid crystalline behaviour is observed (i.e. smectic - nematic, nematic - isotropic transitions). Generally, for a mesophase to exist it is necessary for the termini to contain permanent dipoles. The polarity of the termini frequently gives rise to strong intermolecular forces which stabilise the mesophase formed. However, the polarity of the termini can give rise to adverse effects as the melting points of the compound may be raised so high that the mesophase collapses to the isotropic liquid.

It has been shown that polymorphism may be exhibited by a liquid crystalline polymer upon heating. The presence of polar interactions under these conditions is not the only important factor to be considered for these compounds. It is also necessary to examine the direction of the dipole interactions also. Hence, the stabilisation of smectic states by multiple dipoles acting transversely to the molecular axis (lateral attractions), while terminal attractions appear to be more important in the determination of nematic thermal stability. This is confirmed by the observation that for homologous series, the lower members show purely or predominately nematic ordering, whilst the higher members exhibit smectic mesophases since the ratio of lateral to terminal attractions increases as the series is extended.

The geometrical anisotropy associated with mesogenic compounds is obviously their most common feature. It has already been mentioned that lateral attractions between molecules are important when considering the formation and stability of a mesophase. The size of the lateral substituents must also be considered, and as a rule molecular broadening has a more pronounced effect on the mesophase

stability of smectics than of nematics and the literature is peppered with the effects of molecular broadening and changes in dipole attractions⁴⁸.



Y = End Group	Type
$\text{CH}_3(\text{CH}_2)_n-$	Alkyl
$(\text{CH}_3)_2\text{CH}(\text{CH}_2)_n-$	Branched alkyl
$\text{CH}_3(\text{CH}_2)_n\text{O}-$	Alkoxy
$\text{CH}_3\text{O}(\text{CH}_2)_n\text{O}-$	Dialkoxy
Cl— Br— I—	Halogen
$\text{CH}_3(\text{CH}_2)_n\text{COO}-$	Carboxylic acid ester
$\text{CH}_3(\text{CH}_2)_n\text{OCO}-$	Phenol acidic ester
—CN	Cyano
—NO ₂	Nitro
—NH ₂	Amine, substituted amine

Fig. 4.5 The composition of the terminal groups in some of the aromatic type molecules that exhibit the mesomorphic state.

The abundance of liquid crystalline materials that contain the aromatic ring system may also be attributed to the high thermal stability of the mesophases obtained⁴⁹.

4.3 Aliphatic liquid crystals

Due to the deviation of aliphatic molecules from the required structural criteria for mesomorphism, the number of aliphatic liquid crystals is small in comparison to aromatic systems. However, they do exist and compounds such as monocarboxylic aliphatic acids, palmitates and stearates have been shown to exhibit mesomorphism.

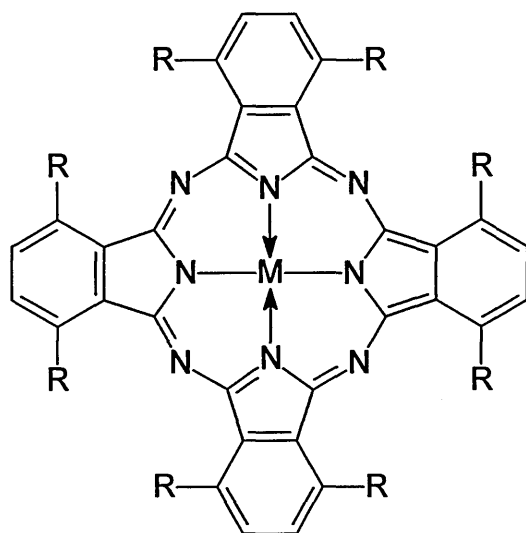
4.4 Homologous series

Extended investigations into the structure - property relationships has led to the synthesis of groups of molecules that differ only by the number of methylene groups incorporated in a terminal substituent. The inability to predict mesophase stability ranges by modelling techniques has led to this type of investigation being the most fruitful. Also, many liquid crystal devices are at present based upon mixtures of mesogenic compounds. In many cases, these mixtures are based upon homologous series used to obtain eutectic mixtures.

However, the study of homologous series has a more fundamental aim. Most molecular structure - property studies involve changes in the polarity of groups, polarisability and molecular geometry. This requires substantial differences to be present within a group of compounds, for example, methyl, cyano and nitro terminal groups impart very different polarity to a given molecule. However, due to the difference in molecular size and shape of these termini, interpretation of their structural effects is difficult. In following a homologous series, only very small changes are made at each step and therefore changes in structure - property relationships can be more clearly attributed. This was demonstrated by Grays' studies⁵⁰. These showed that when the mesomorphic transition temperatures for a homologous series of compounds were plotted against the number of carbon atoms in the alkyl chain, e.g. in a homologous series of n-alkyl ethers, a smooth curve relationship for like transitions was found. To an extent this is true for mesophase to mesophase transitions, but deviations can occur due to the complex molecular attractions that can occur.

4.5 Discotic liquid crystals from mesogenic phthalocyanines

Over recent years a new series of phthalocyanine derivatives with purpose designed substitution patterns has been developed. The synthesis of some of these has been stimulated by an interest in devising structures that generate liquid crystalline phases. Examples of these mesogenic phthalocyanines generally fall into two broad categories depending upon the location of the substituents about the ring. The peripherally substituted compounds bearing typically eight long chain substituents at the 2, 3, 9, 10, 16, 17, 23 and 24 positions, constitute the first category and have been extensively investigated⁵¹⁻⁵³. The second category studied are a series of non-peripherally substituted derivatives (Fig. 4.6), where the substituents are located at the 1, 4, 8, 11, 15, 18, 22 and 25 sites. Both the metal free and the metallated species have been shown to exhibit liquid crystalline behaviour⁵⁴⁻⁵⁸ and show mesophases which have been identified as columnar discotic in nature.



1. R = Alkyl; M = H, H or Cu, Zn, Ni
2. R = CH₂O alkyl; M = H, H or Cu

Fig. 4.6 Non-peripherally substituted mesogenic phthalocyanines.

Further studies have been undertaken to examine the effect of reduction of symmetry within the phthalocyanine molecules on the exhibited liquid crystalline behaviour. The incorporation of unsymmetry into the phthalocyanine has been achieved by the stepwise base catalysed

cyclisation of the appropriate phthalonitriles⁵⁹ to produce the structures illustrated below (Fig. 4.7i and ii.). Compounds of type i. exhibited discotic mesophases regardless of the reduction in alkyl chains compared with the molecule illustrated in Fig. 4.6. The incorporation of a side chain functionality into the type ii. phthalocyanine provided a degree of amphiphilic character to the molecule, discotic liquid crystalline mesophases were also observed for this system.

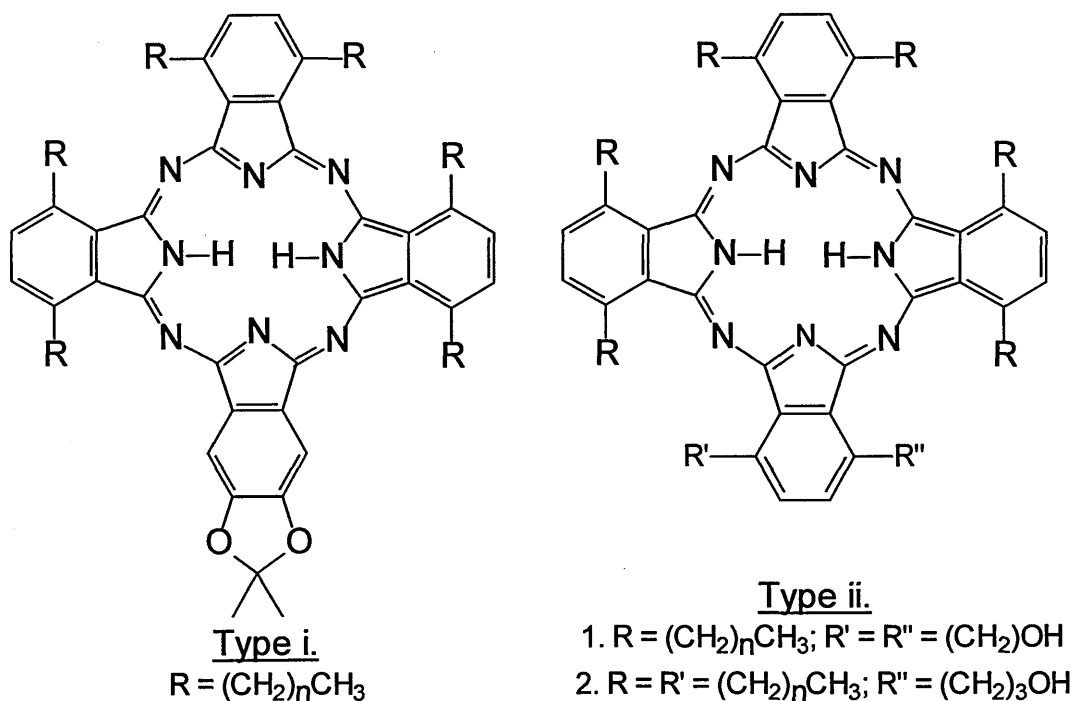


Fig. 4.7 Unsymmetrical non-peripherally substituted mesogenic phthalocyanines.

5 Polymer liquid crystals

Liquid crystalline polymers are high molecular mass materials, containing repeating sub-structures, which exhibit mesomorphism. Traditionally the occurrence of such materials has been in one of two states, either the liquid crystal main chain polymer or the liquid crystal side chain polymer (although other macromolecular systems have been identified, notably the combined liquid crystal polymers and the rigid rods). The study of liquid crystal properties in polymer systems has afforded new knowledge on both the polymeric system and the mesophase⁶⁰

5.1 Thermotropic liquid crystalline polymers

5.1.1 Main chain liquid crystalline polymers

The design and synthesis of liquid crystalline polymers that incorporate suitable mesogenic groups as part of the polymer backbone can be achieved by consideration of the structural requirements of liquid crystals previously discussed (section 4). By the connection of suitable mesogenic monomers and a linking entity, a polymer backbone can be created which is connected by suitable functionalities situated at each end of the mesogenic monomer. Synthesis usually proceeds via a condensation reaction to form a polymer of the type illustrated below (Fig. 5.1)

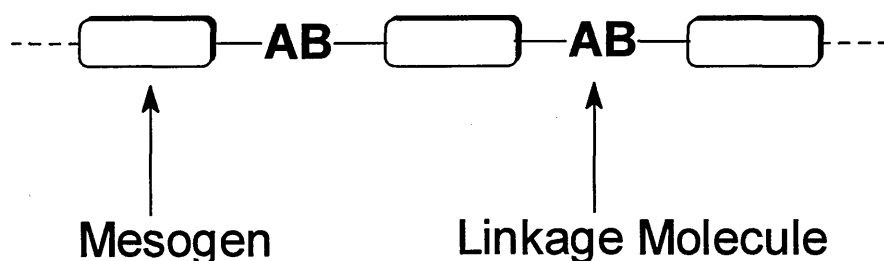


Fig. 5.1 Main chain thermotropic liquid crystalline polymer.

The linkages between A and B and the mesogens may be direct giving a rigid polymer backbone (c.f. biphenyl), or be of a more flexible nature which affords a polymer that contains an alternating series of rigid and flexible units. Both of these are described as liquid crystalline main chain polymers and each preserves the original liquid crystalline moieties of the monomers. This suggests that the mesogenicity of the monomer can be preserved in the polymer chain, and there are many examples of this being the case, although a *polymer effect* leads to changes in the absolute thermal parameters.

5.1.1.1 Synthesis of main chain liquid crystals

Main chain liquid crystalline polymers are normally synthesised by step-growth reactions, such as condensation. In this type of polymerisation, the reactant monomers usually contain two functional groups. Suitably substituted mesogenic compounds may be used but it is also possible to use non-mesogenic compounds. The mesogenic segment of the polymer chain is created from these monomers during the polymerisation process. If a high molecular weight material is required then the functional groups are limited to those which may be used in procedures involving high yield reactions⁶¹. This generally requires the use of polymerisation procedures that create polyester or polyamide systems, which tend to be high molar mass materials. In fact it was the practical application of lyotropic polyamides in the form of Kevlar[®], obtained by the solution spinning of an aromatic polyamide in the lyotropic state, that provided the incentive for the initial research into the area of main chain liquid crystalline polymers. A study of the historical development of polyamides and other similar molecular systems has shown that mesomorphism is exhibited by those structures that retain the linearity and rigidity of the *p*-phenylene group⁶²; thus, e.g., the *p*-phenylene groups may be connected by *trans*-azo or *trans*-vinylene groups and still retain their rigid, and approximately linear conformations.

As previously discussed the mesogens may be connected either directly or via semiflexible units. The different models are shown schematically below (Fig. 5.2)

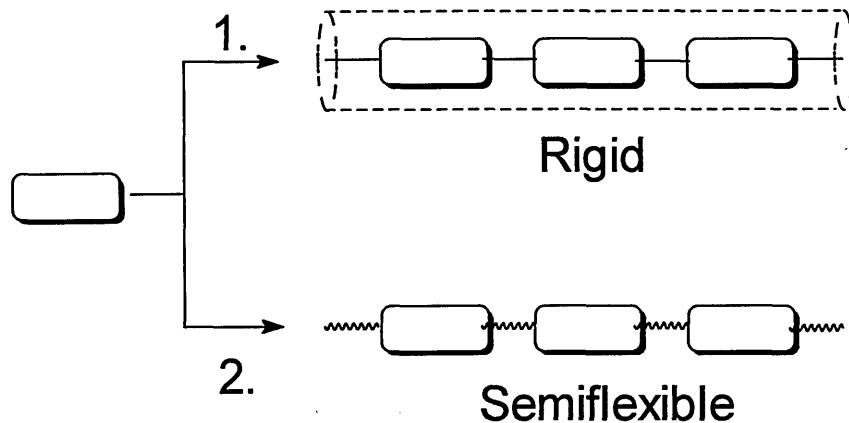


Fig. 5.2 Schematic structure of liquid crystalline main chain polymers. 1. Directly connected mesogens form a rigid rod-like polymer. 2. Mesogens are connected via flexible linkages.

(1). Rigid main chain polymers

A large number of polymers containing a rigid rod-like main chain have been prepared and are documented in the literature⁶³. One of the best known examples of a polymer of this type that has a commercial application is Kevlar[®].

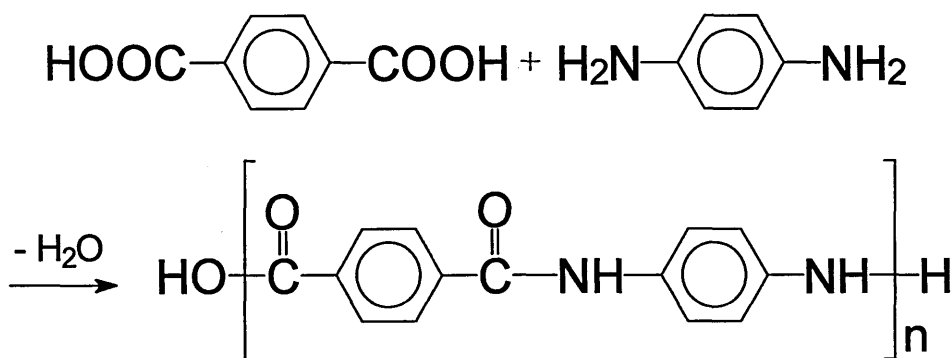


Fig. 5.3 Reaction scheme for the preparation of Kevlar[®].

The polymer is formed by the condensation of terephthalic acid and *p*-phenylenediamine to form the polyamide illustrated (Fig 5.3). Although the material is infusible and cannot therefore exhibit thermotropic mesomorphism, it is soluble in concentrated sulphuric acid in which a nematic phase occurs. The phase may be processed in such a way that highly oriented fibres may be prepared from the material.

This example demonstrates that polymers that are rod-like with a symmetrical structure are unsuitable for obtaining thermotropic mesophases since decomposition occurs prior to the event. As the number of repeat units, n , in the polymer increases so the difference between the melting point and the decomposition temperature increases. The problem posed by the high temperatures that are required to transform the polymer from the crystalline to the mesomorphic phase can be approached in two ways, both involving modifications to the main chain of the polymer. Firstly, the linearity of the polymer backbone may be reduced by the introduction of non-linear yet rigid components, and this has the effect of deforming the cylindrical shape of the polymer. As the amount of the non-linear comonomer unit increases, the melting point of the polymer decreases due to the loss of order caused by the reduction in stacking efficiency of the molecules.

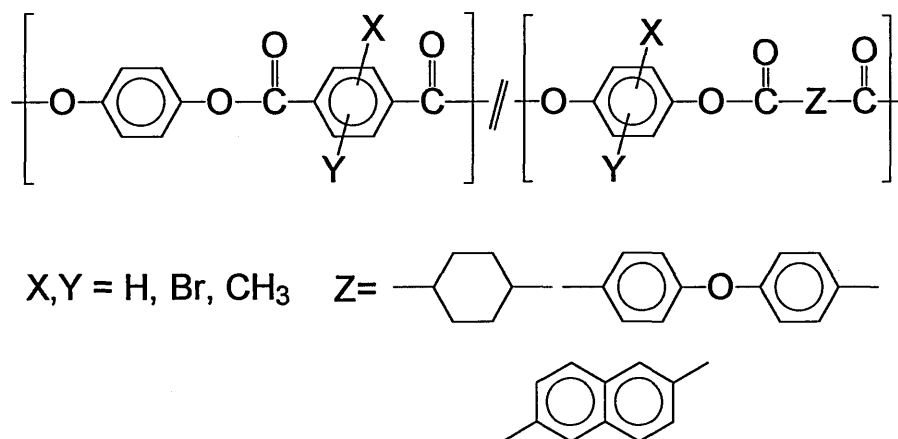


Fig. 5.4 Examples of copolymers that contain non-linear monomer units⁶⁴.

At a certain level the melting point falls below the decomposition temperature and thermotropic liquid crystallinity is observed. Examples of copolymers that contain non-linear monomer units are shown above (Fig. 5.4).

The substitution of lateral alkyl chains onto the mesogenic monomer units provides the second possibility, these acting as lubricants between the rod-like polymers. This concept has been successfully applied to cellulose derivatives which become thermotropic liquid crystals when they contain long-chain, lateral substituents⁶⁵.

(2). Semiflexible main chain polymers

The problems of high melting points in polymers that contain only rigid, rod-like segments may be overcome by the introduction of flexible moieties like alkylene or alkyleneoxy chains into the main chain of the polymer. A variety of polymeric systems is conceivable by altering the chemical structures of the mesogens, the lengths of the flexible spacers or the number of different monomer units in the copolymer⁶³.

5.1.1.2 Phase behaviour related to molecular structure.

Liquid crystalline main chain polymers have been found to exist in all of the common mesomorphic states i.e. nematic, cholesteric and smectic. The relation between phase behaviour and molecular structure is complex due to the polydispersity of the material which is determined by the polymerisation process. This is in contrast to lyotropic liquid crystalline materials where, in a homogenous mesophase of one component, all molecules have the same size or molar mass⁶⁶.

Consideration of the structure of rigid, rod-like polymers allows the basis for the formation of nematic mesophases to be understood (Fig. 5.5 a.).

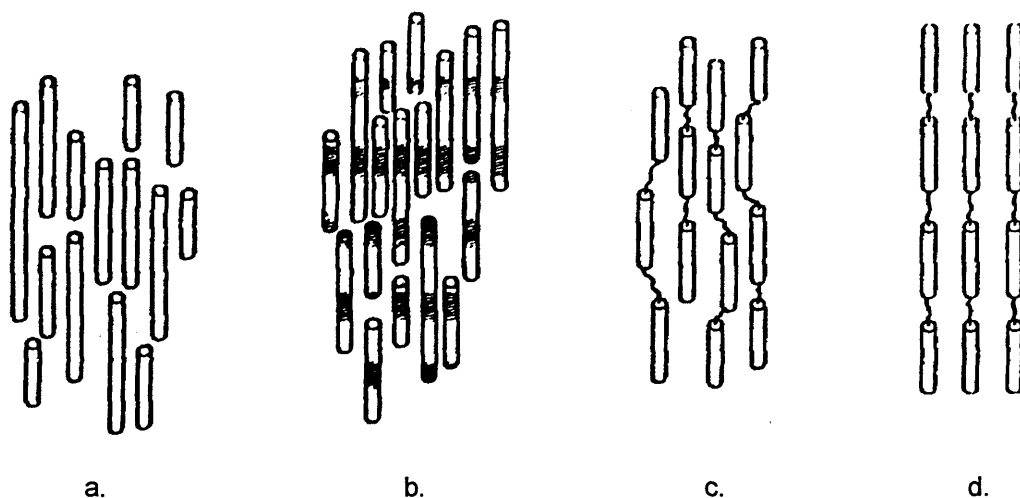


Fig. 5.5 Nematic and smectic phases of rigid rod and semiflexible polymers.

Essentially, the length and polydispersity of the rod-like macromolecules causes a statistical arrangement of the centres of gravity which causes the nematic ordering of the molecules. For a smectic phase to occur the polymer should consist of an ordered sequence of monomer units to allow for an ordered arrangement about the centres of the monomer units (Fig. 5.5 b.). It therefore follows that the formation of smectic phases is suppressed and the formation of nematic phases promoted in statistically irregular copolymers and polymers with non-linear backbones and laterally substituted monomer units.

In semiflexible main chain polymers, the flexible spacer allows some freedom to the mesogenic moieties resulting in a pronounced effect on the stability of the mesophase formed. In homopolymers where there is a regular sequence of rigid, mesogenic moieties and flexible spacers, the structure of the mesophase is determined by the mesogens within the main chain (Figs. 5.5 c. and d.). Short flexible spacers favour nematic mesophases, whilst longer spacers favour the smectic phase. In statistically irregular copolymers where the lengths of the mesogenic moieties or the lengths of the spacers may vary a nematic mesophase is generally observed.

5.1.2 Side chain liquid crystalline polymers⁶⁷

As the name suggests, side chain liquid polymers are quite simply polymeric materials that carry the mesogenic moieties as side chains. These are generally synthesised by a polymer modification reaction that involves the hydrosilylation of mesogenic alkenes onto the backbone of siloxane polymers (see section 5.1.2.1 c), this creates a polymer backbone with the mesogens as the pendant side chains (Fig 5.6).

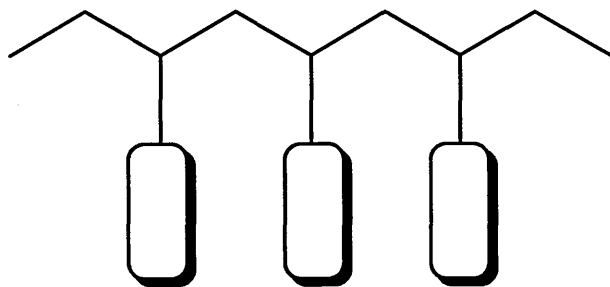


Fig. 5.6 Structural representation of a typical side chain liquid crystalline polymer.

There is the possibility of the mesogenic units being attached directly to the polymer backbone or via flexible spacers, alkyl chains for example. This in fact is the a crucial factor in the design and synthesis of side chain liquid crystals. Direct linkage except in a few cases⁶⁸ gives only glasses with an anisotropy of structure that is lost at the glass transition temperature. Coupled with the steric interactions between the side chain groups , the tendency towards a statistical distribution of the chain conformations hinders the ordered arrangement of the pendant groups and liquid crystallinity in the polymer is suppressed. The side groups may be significantly decoupled by the introduction of a flexible spacer between the main chain and the pendant group, this allows the main chain motions to occur without disturbance of the anisotropic arrangement of the side chains. The polymer may then exhibit liquid crystalline characteristics and mesophases may occur.

5.1.2.1 Synthesis of side chain liquid crystals

Liquid crystalline side chain polymers consist of two components, the mesogens themselves and the polymeric main chain to which they are attached. The spacers are thought to contribute to the characteristics of both components. A wide variety of both mesogenic moiety and polymer main chain are available thus the combination of these components allows many different types of mesogenic side chain polymers to be prepared. The synthesis of liquid crystalline side chain polymers follows polymerisation procedures that are well established in polymer chemistry (Fig. 5.7).

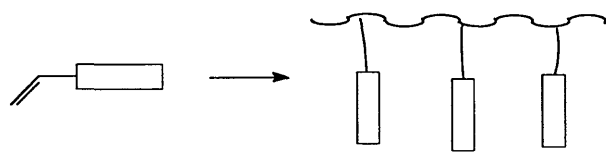
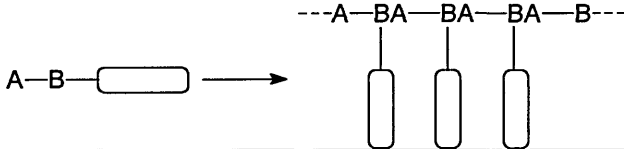
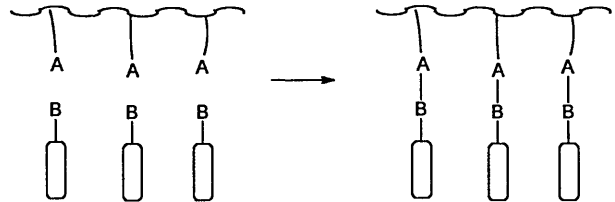
Principle	Reaction	Examples
Addition Polymerisation		Polyacrylates Poly-methacrylates Polystyrene Derivatives
Condensation Polymerisation		Polyesters
Modification of Polymers		Polysiloxanes

Fig. 5.7 Methods for the synthesis of side chain liquid crystalline polymers.

It is possible to apply both step-growth reaction (e.g. polycondensation reactions) or chain-growth reactions (e.g. radical or ionic addition polymerisation) to the formation of mesogenic side chain polymers with the only limitations being the occurrence of side reactions, such as chain transfer or reactions involving the initiator and mesogenic functionalities. The modification of polymeric materials by the attachment of mesogenic units to create liquid crystalline side chain polymers is also a viable method and leads to the important polysiloxane liquid crystal polymers.

(a) Chain-growth reactions

This is a frequently used polymerisation procedure for the preparation of side chain liquid crystal polymers and involves the radical initiated polymerisation of mesogenic monomers (Fig. 5.8). Typical systems are based upon derivatives of acrylic or methacrylic acid with mesogenic moieties such as substituted benzoic acid phenyl esters, aromatic azo or azoxy compounds, aromatic Schiff bases, biphenyls and cholesterol⁶⁹.

(c) Polymer modification

Formation of side chain liquid crystalline polymers may be achieved by polymer modification using polymers which contain a functional group in the repeating unit⁷¹. An example of this type is the smooth addition of vinyl substituted mesogenic monomers to poly(hydrogenmethylsiloxane) (Fig. 5.10), commonly known as the hydrosilylation of alkenes.

The procedure for the hydrosilylation of alkenes involves the addition of a Si-H bond, e.g. of a poly(hydrogenmethylsiloxane), across the double bond of an alkene. The reaction is normally catalysed by Pt(II) but care must be taken with the quality of the catalyst otherwise side reactions are probable.

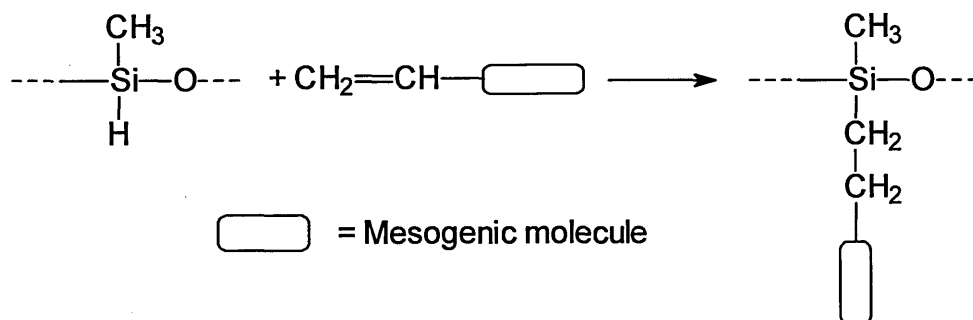


Fig. 5.10 Polymer modification for the formation of side chain liquid crystalline polymers.

5.1.2.2 Relationships between phase behaviour and molecular structure for side chain liquid crystalline polymers

The characterisation of liquid crystalline side chain polymers analyses a combination of both polymer specific and liquid crystal specific properties. In comparing the phase behaviour of the mesogenic monomer with that of the polymer two important changes are observed-

- The increased tendency towards the formation of smectic phases.
- The increased liquid crystalline phase transformation temperatures of the polymers⁷².

The increased tendency for the formation of smectic phases can be explained by the reduced mobility of the mesogenic side chains, which are connected to the polymer backbone. This results in a reduction in the rotational and translational motions associated with the molecule, and as a result the formation of a smectic state is favoured. This is particularly noticeable in polymers that lack a flexible spacer between the main and side chains, in these cases either no liquid crystalline phase is obtained or a smectic phase is obtained. The presence of a long spacer chain also may favour the formation of smectic mesophases, but this is often in addition to the formation of crystalline and nematic phases. These smectic polymers are characterised by high clearing temperatures and high glass transition temperatures⁷³. Stiffening of the backbone by the mesogens results in high T_g values for the side chain polymer compared with the corresponding unsubstituted polymer.

5.3 Characterisation of thermotropic liquid crystalline polymers

The characterisation of liquid crystalline polymers is usually via a comparison of the mesophase transitions. The mesophases are commonly characterised in terms of the types of structural transition they exhibit and the temperatures at which these transitions occur. Studies involve the examination of materials using techniques such as thermal microscopy and differential scanning calorimetry; x-ray methods may also assist.

5.3.1 Differential scanning calorimetry

The essential features of the phase behaviour of liquid crystalline side-chain polymers are well established⁷⁴. Commonly, a DSC trace will contain various features as follows-

- A glass transition that is characteristic of the polymer backbone.
- A glass to mesophase transition.
- A transformation from the mesophase to the isotropic phase due to the mesogenic side-chains.

Studies of liquid crystalline side-chain polymers have resulted in the identification of systematic trends that exist between liquid crystal phase behaviour and changes in molecular structure. This suggests that changes in molecular structure and molecular weight have a pronounced effect on the thermal stabilities of the mesophases themselves. It has previously been discussed that the attachment of mesogenic side groups, via flexible spacers of the same length, to different polymer backbones results in a liquid crystalline mesophase that exhibits a reduced thermal stability with an increase in the flexibility of the polymer main-chain⁷⁴. Thermal studies of liquid crystalline polymers compared with their corresponding monomers show a stabilisation of the mesophase for polymeric materials as well as a shift in the phase transition of the polymers to higher temperatures.

Liquid crystalline main-chain polymers exhibit a far more complicated thermal behaviour. Multiple transitions may be exhibited and commonly include a glass transition and a melting (endotherm), as well as mesophase-mesophase and mesophase-isotropic liquid transitions (endotherms).

Rapidly *quenched* samples may demonstrate the so-called cold crystallisation (exotherm) when reheated above the glass transition temperature⁷⁵. However, for low molecular weight materials, the cooling rate has a pronounced effect on the behaviour of the material at low temperatures⁷⁶. Slower cooling rates result in smaller glass transitions and cold crystallisation exotherms. At lower temperatures additional transitions may be observed⁷⁷ which occur as a result of-

- Recrystallisation of the polymer chains during the melting of the original crystalline structure. The implication of this is the co-existence of two interconvertible forms of polymer that differ only in terms of crystal size and perfection.
- Differences in chain morphologies. The morphologies are assumed to be so different that no structural changes occur during the thermal scan, and as a consequence the melting endotherms obtained are assumed to be dependent only on the initial structure of the material.
- Polymorphism.

These effects render the interpretation of DSC curves for liquid crystalline main-chain polymers difficult, and the nature of transitions are usually established by a combination of thermal studies, optical observations and X-ray studies.

Chapter 3

Organic Conductors

1. Introduction

During the last 25 years there has been a rapid development in the syntheses and characterisation of novel organic conductors, which exhibit high or metallic like electrical conductivities. While the understanding of the mechanism of electrical conduction in such systems may be compared to that of inorganic semiconductors, the opportunity for *tailoring* the electrical properties of a material through the utilisation of synthetic organic chemistry has been a major driving force for extensive research activity.

For many years, it has been possible to develop a wide range of mechanical properties in organic solids through the preparation of specific molecular structures. The extension of this technique to the control of electrical properties has since allowed the scope of semiconductor applications to be expanded.

A primary motivation for the research activities into the development of organic semiconductors has been the potential technological applications that these substances may possess. The primary aim of this research has been the isolation and development of a high temperature superconductor, which may be defined as a material which exhibits a complete lack of electrical resistance below a certain critical temperature. The industrial potential for materials exhibiting superconductivity is indeed extensive when the potential applications are considered, for example-

- Increased efficiency in electrical power transmission.
- Increased efficiency in electrical motors.
- The possibility of more powerful and efficient computers.

The application of organic materials as conducting solids is of interest in respect of the properties and fabrication of the material. Comparisons may be made with both metals and ceramics, thus enabling the identification of key areas in which organic materials have advantageous properties, for example-

- Low density compared to metals.
- Potentially cheaper and simpler to fabricate into materials by comparison with ceramics.
- Possibility of polymeric systems that may be compatible with both biological systems and with familiar engineering materials.

It should be noted that materials do exist that exhibit superconductivity; however extreme cryogenic temperatures are generally required and consequently the costs of maintaining superconducting conditions are prohibitive.

Synthetic organic semiconductors generally fall into two major classes; molecular crystals and polymers. The classical example of a semiconducting molecular crystal is anthracene^{78,79} (Fig 1.1).

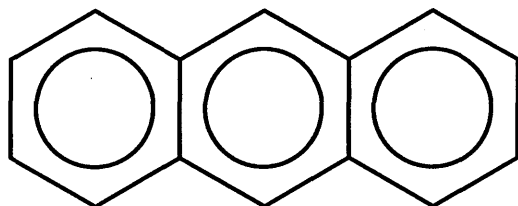


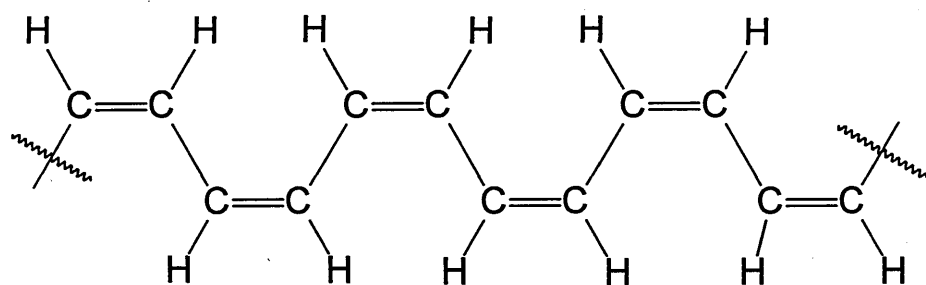
Fig 1.1 Molecular structure of anthracene.

In the crystalline state, anthracene exists in structured layers and is capable of exhibiting dark dc conductivity⁸⁰. The unit cell is monoclinic and contains two molecules.

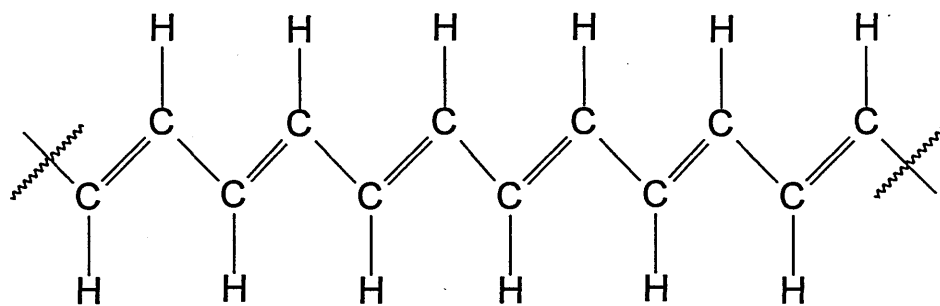
The potential applications of semiconducting polymers are extensive as it is desirable to have a material in which the electrical conductivity could be variably controlled, whilst exhibiting characteristics that facilitate ease of processability. This would lead to a successful mouldable

conductive material which would combine the excellent electrical properties of a metal with the processing ease of a polymer. This area of research led to the discovery of the semiconducting characteristics of doped polyacetylene⁸¹⁻⁸⁵ (Fig 1.2), which will be discussed later in this chapter.

The semiconducting properties of polymers and similar organic materials are not nearly as well defined as those of molecular crystals, partly due to the lack of physical/chemical structural characterisation of the polymers compared with the molecular crystals.



CIS



TRANS

Fig 1.2 Cis and trans molecular structures of polyacetylene.

2. Semiconductors

2.1 The conduction process

The most important characteristic about semiconductors is quite simply their ability to allow the passage of electrical current. The current is dependent on both the number of charges free to move and the speed at which they move. An important consideration is that the currents generally measured are the results of motions of a large number of individual charge carriers and not the component current produced by the motion of any one charge.

The ability of materials to conduct electricity may be explained by the use of band gap models to describe the energy levels resulting from the combination of appropriate molecular orbitals for the material, and the situation of the electrons⁹ (Fig 2.1).

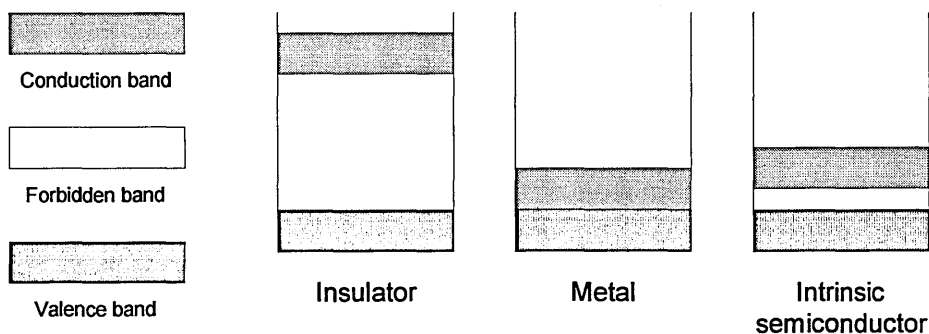


Fig. 2.1 Schematic band models of solids classified according to their electronic properties.

The theory most often used to describe the way electrons bind nuclei together to form molecules is the *molecular orbital theory*. The association of molecules to form a new molecular material is achieved by the combination of molecular orbitals (from the original component species). This combination of molecular orbitals may occur in phase to give a bonding molecular orbital, or out of phase to give an anti-bonding molecular orbital. The bonding molecular orbital is lower in energy than the original molecular orbitals, and the antibonding molecular orbital higher in energy. The amount by which the energy is reduced for the bonding molecular orbital is dependent on the amount of overlap of the component molecular orbitals; for example a decrease in the overlap results in a decrease in

the energy difference between the original and bonding molecular orbitals. At the simplest level, if we consider a hypothetical molecule, M, that contains one bonding and one anti-bonding molecular orbital for the component molecule, where ΔE is the energy gap between them, it is found that for successive additions of molecules to the lattice-

1. The energy separation between the lowest energy bonding molecular orbital and highest energy antibonding molecular orbital does not greatly increase (remains at approximately ΔE).
2. New molecular orbitals are situated in the gap between the two original molecular orbitals (Fig. 2.2).

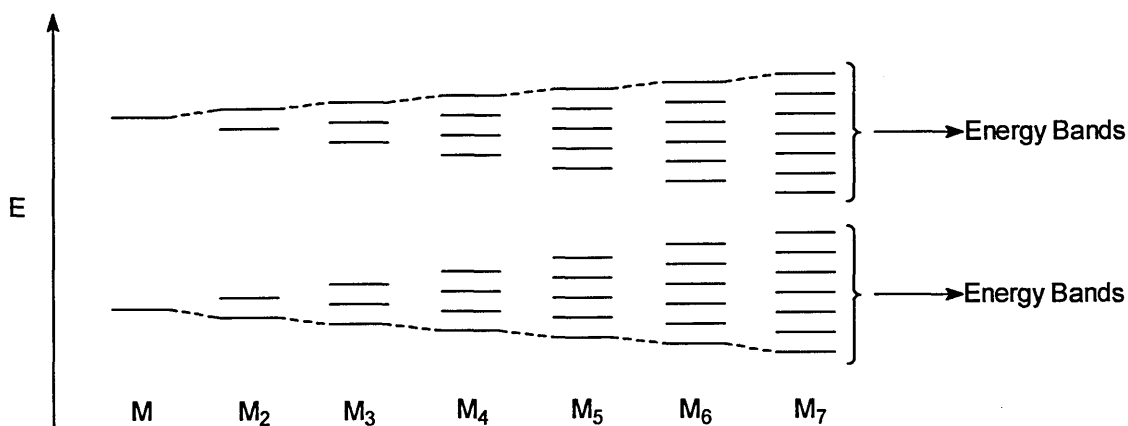


Fig. 2.2 Orbital energies for a chain of molecules, M of increasing length.

As stated above, it may be noted from the diagram that as the chain length increases the number of levels increases but the spread of energies seems to increase only very slowly. For extremely long chains, it may be seen that a very large number of levels exist within a comparatively small range of energies. The range of energy levels is in fact so small that the set of levels may be thought of as a continuous range of energies known as an *energy band*.

Comparison of the energy level diagrams of different molecular structures gives an insight into the electrical properties that are exhibited. The energy required for the $\sigma\text{-}\sigma^*$ transition of an electron is much greater than the $\pi\text{-}\pi^*$ transition ($\Delta E_{\sigma\text{-}\sigma^*} \gg \Delta E_{\pi\text{-}\pi^*}$). Consequently, saturated systems tend to have

a large band gap and exhibit insulating or semiconducting electrical properties. Within π systems there is often the potential for narrow or non-existent band gaps which can allow access to the band levels above the Fermi level (E_F). The Fermi level is the highest occupied energy level in the ground state. In accordance with conventional band theory, electrons in levels above the Fermi level are not bound to the lattice and may therefore act as charge carriers for electrical conduction.

Thus, conductors are characterised either by the partial filling of bands or by an overlapping of the topmost bands. Conversely insulators have completely filled lower bands with a wide energy gap between the topmost filled band and the lowest empty band. The range of conductivity values shown below (Fig. 2.3) illustrates the classification of materials according to their ability to conduct electrical charge.

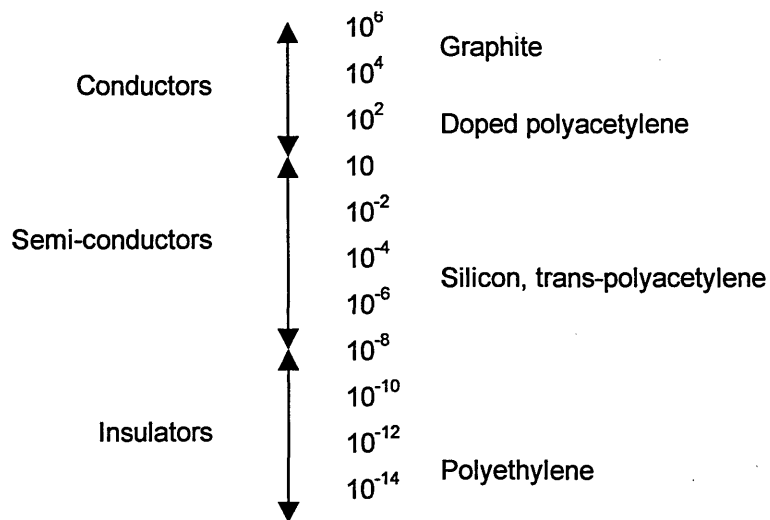


Fig. 2.3 Illustration of the conductivity values ($\Omega^{-1}\text{cm}^{-1}$) for a range of materials.

2.2 Semiconductors

Two types of semiconductivity may be exhibited by a material; these are known as intrinsic or extrinsic semiconduction.

2.2.1 Intrinsic semiconduction

A semiconductor is a material that shows an increase in electrical conductivity as the temperature is increased, (in a metal the opposite is true as an increase in temperature results in an increase in the vibrations of the ions in the crystal lattice, which interferes with the motion of the delocalised electrons, hence reducing conductivity). In an extremely pure form semiconductors exhibit what is known as intrinsic semiconductivity, this is essentially the facilitation of electrical conduction by means of electrons which are present only by virtue of the material itself and not the presence of any contaminants. Examples of this type are pure silicon or germanium.

Upon examination of the energy band structure of intrinsic semiconductors it is possible to see a similarity with insulating materials, the obvious difference being the smaller size of the energy gap between the valence and conduction bands in semiconducting materials (Fig 2.1). Electrons in a completely filled valence band can make no contribution to the overall conductivity of the material. Thermal excitation of the valence electrons in a semiconductor may result in the promotion of electrons to the conduction band. As soon as holes are formed in the valence band the remaining electrons are able to make a contribution to the conductivity by migration between vacant sites. A hole in a band of negative electrons may be considered essentially as a point of positive charge and the jump of an electron into a vacant hole is equivalent to the jump of a positive charge into the position vacated by the electron. We can therefore treat the motions of electrons in an almost filled band as if the holes were positive charges moving in an almost empty hole band.

2.2.2 Extrinsic semiconductors

As previously explained, the thermal excitation of electrons across the band gap of a material results in the exhibition of semiconductivity. However, for most practical semiconductors the electrical conductivity is controlled chiefly from thermal excitation by localised imperfections. Since the density and ionisation energy of these imperfections may be varied by the choice of different additives (*dopants* that may be either electron donors or electron acceptors), a large degree of variation is made possible by this use of *extrinsic* semiconductivity.

The simplest kind of additives or contaminants (that cause lattice imperfections) are those that differ in valency by one in comparison to the atom for which they substitute. Such imperfections generally provide new energy levels that are close to either the conduction or valence bands. Additives donate electrons to the conduction band if the number of their valence electrons exceeds those of the atom for which the additive is substituting. The impure or *doped* semiconductor is called *n-type* because the negative charges are responsible for an increase in conductivity. Imperfections accept electrons from the valence band if the number of their valence electrons is less than those of the atom for which the imperfection is substituting. In this case the enhanced conduction is primarily due to the positive holes and the doped semiconductor is designated *p-type*.

2.2.3 One dimensional organic semiconductors

There are many examples of one-dimensional organic semiconductors. For instance the uses of transition element - macrocyclic ligand complexes⁸⁷ and organic charge transfer molecules⁸⁸ have been studied extensively.

One-dimensional organic semiconductors are produced by the partial transfer of an electron from a donating molecule of low ionisation potential to an electron accepting molecule of high electron affinity⁸⁶. It must be stressed that it is only the non-stoichiometric transfer of electrons that gives rise to relatively highly semiconducting solids.

After the partial transfer of charge, the subsequent consideration for a one-dimensional organic semiconductor is that of crystal structure. High conductivity is associated with a crystal structure that exhibits a stack of donor molecules with an adjacent stack of acceptor molecules (Fig. 2.4). This configuration of molecules is known as *segregated stacking*.

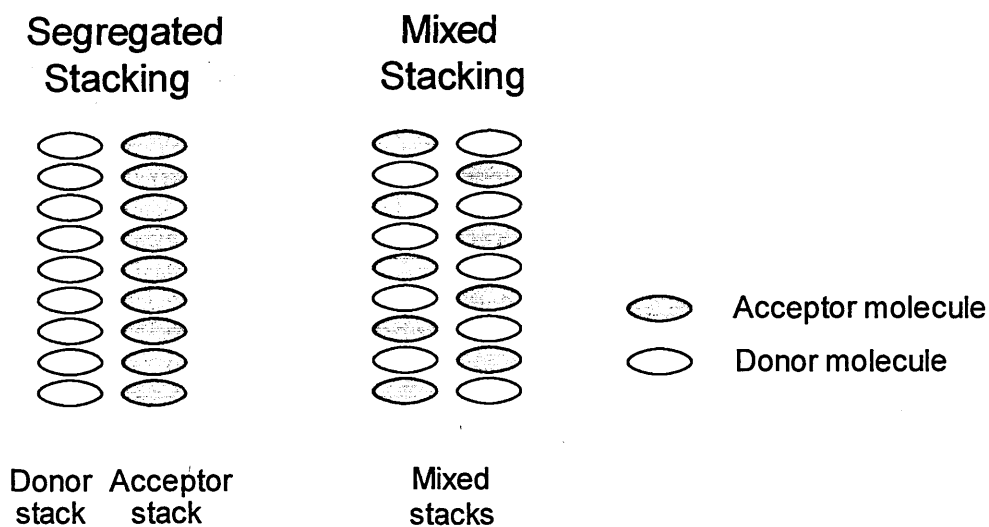


Fig. 2.4 Illustration of the molecular stacking exhibited by one-dimensional organic semiconductors.

There is no conclusive reason why segregated stacking should arise, but it is generally accepted that segregation yields more highly conductive materials than one dimensional organic semiconductors of mixed stacks with alternating donor and acceptor species^{86,88-90}; the explanation of this will be given after consideration of the orbital overlap within the stacks. Stacking may not be direct but may involve displaced or tilted molecules within the stacks.

The final requirement for conduction to be exhibited is the existence of a conduction path along the molecular crystal. Such a path would occur if the molecules formulating the stacks possess delocalised π -orbital electrons over the carbon skeleton in orbitals which are able to overlap with the π -orbitals of adjacent molecules in the stack thus leading to long range overlap throughout the stack. As a consequence, anisotropic conductivity occurs along these delocalised electron orbitals and gives rise to the term 'quasi one-dimensional organic conductors'. The lack of orbital overlap expected within mixed stacks can now be seen as the reason for the formation of more highly conductive species by segregated stacking. Since conduction cannot occur through the π -orbitals, conduction may only occur by the *hopping* of electrons or holes BETWEEN stacks. This leads to a material of high resistance.

In summary, the prerequisites for high conductivity in a charge transfer complex are-

- Partial charge transfer from donor to acceptor stacks.
- Segregated stacks of donor and acceptor molecules.
- Delocalisation of π -electron orbitals within the stacks.

Other factors that may contribute to increased conductivity are-

- Lack of solvent inclusion in the molecular crystals.
- Donor and acceptor species of a similar size and geometry.
- Uniform intermolecular spacing, regular overlap of orbitals.
- Planar molecules with significant π densities.

Electrical conduction can therefore occur due to the transfer of electrons from the donor to the acceptor stack. Once in the acceptor stack, conduction proceeds through the stack in a one-dimensional direction via the delocalised π -electron orbitals of adjacent molecules. Alternatively, conduction can occur via the holes that remain in the donor stack. In either case the number of charge carriers will depend on the relative donor and acceptor powers of the components.

3. Synthetic organic semiconductors

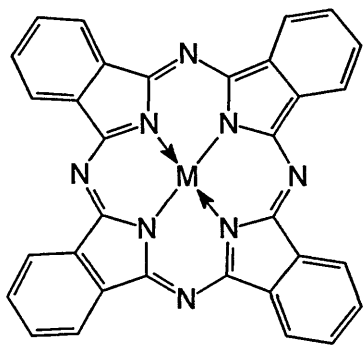
There are currently many areas of research interest in the field of synthetic organic semiconductors. Ongoing development is being carried out in the areas of organic charge transfer complexes, novel superconductors, conductive organic polymers, Krogmann salts and related materials, transition element macrocyclic ligand complexes and polymer-salt complexes. All of these are well documented⁸⁷, but it has been our research into polymeric and macrocyclic Schiff's bases that has led us to consider electrical conductivity as a second point of interest (c.f. liquid crystals) in the study of the materials reported in this work. Accordingly the following sections concentrate on macrocyclic and polymeric conductors.

3.1 Transition element - macrocyclic ligand complexes

The development of transition element - macrocyclic ligand complexes as conductive molecular solids has been in progress since the 1970's. These materials which solidify as stacks of metallomacrocyclic molecules, become conductive when oxidised with for example I_2 or Br_2 . This produces lattices which contain one-dimensional arrays of planar donor molecules with fractionally occupied electronic valence shells. The assumption of a partial oxidation state by the metal cation radical in the stacks of the metallomacrocyclic results in the parallel formation of polyhalide ions in the

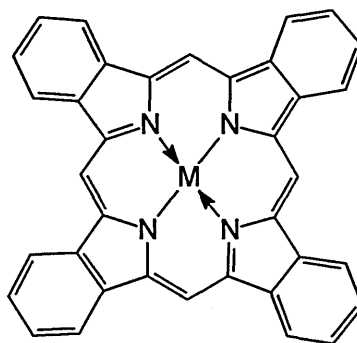
structure. The types of macrocyclic structure that exhibit this type of behaviour are illustrated below

(Fig 3.1).



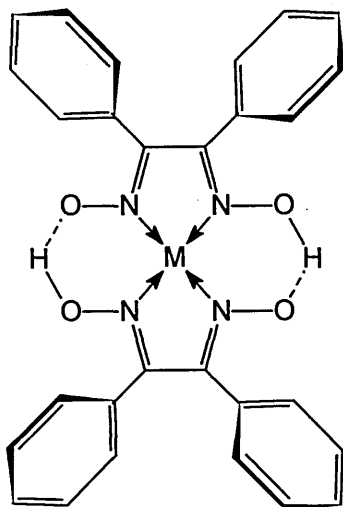
Phthalocyanine

(M= Fe, Co, Ni, Cu, Zn, Pt)



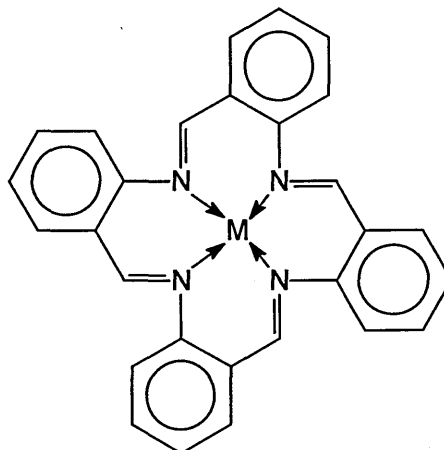
Tetraphenylporphyrin

(M= Ni, Cu, Pb, Zn, Sn)



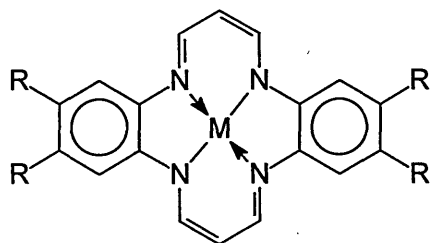
Bis(diphenylglyoximate) metal(II)

(M= Pd, Ni)



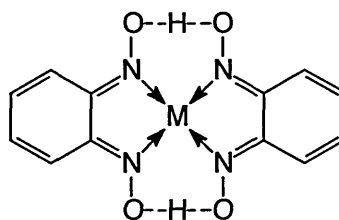
Tetraazacyclohexadecine

(M= Pd, Pt)



Dibenzotetraaza[14]annulene

(M= Pd, Ni, Cu, Co)

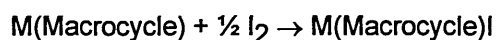


Bis(o-benzoquinonedioximate) metal(II)

(M= Pd, Ni)

Fig. 3.1 Transition element - macrocyclic ligand complexes.

The general oxidation process in these complexes follows the equation-



Data obtained from resonance Raman, Mössbauer (iodine), x-ray diffuse scattering, electron spin resonance, magnetic susceptibility, and charge transport measurements indicate that the iodine or bromine moieties are polyhalide species (I_3^- , I_5^- , Br_3^- , Br_5^-). As a consequence, the formal oxidation state of the metal is retained and thus plays only a secondary role in the conduction process, whilst the charge carriers are associated with the delocalised π -orbitals on the macrocycle itself. Therefore, the electron charge carriers are associated with the ligand π -system and not with the metal itself.

When considering the utilisation of the halogens as oxidising species for the formation of semiconducting complexes of this type there must be consideration of the halogenic species used in this procedure. The high capability of the halogens to accept electronic charge from donor molecules is related to the oxidising power of the halogens themselves (i.e. $F_2 > Cl_2 > Br_2 > I_2$). However, the less powerfully oxidising halogens are of greater value in terms of the ease of formation of polyhalide chains.

3.1.1 Diphenylglyoximates

The tetragonal structures of metal-halogen-diphenylglyoxime derivatives, $[M(\text{dpg})_2X]$ have been studied from as early as 1967⁹¹. Conducting stacks are formed by square coplanar $M(\text{dpg})_2$ units which form columnar stacks with equivalent M-M distances. The halogen atoms are situated in channels which run parallel to the metal chains and are surrounded by the phenyl groups of the ligand. The halogenic oxidation of the diphenylglyoximates increases the conductivity of the materials by about six orders of magnitude.

3.1.2 Bis(benzoquinone)dioximates

Bis(benzoquinone)dioximates (bqd) are closely related to the diphenylglyoximates⁹². The existence of a quasi-one-dimensional material of stoichiometry $M(\text{bqd})_2\text{I}_{0.5}$ ($M = \text{Ni}$ or Pd) was established by Endres^{93,94} and it was noted that in some cases the incorporation of solvent molecules into the lattice was observed. Electrical conductivities for some bis(diphenyl)glyoximates and bis(benzoquinone)dioximates are given in Fig. 3.2⁹⁵, and they illustrate the effect of the halogenic oxidation and the inclusion of different solvent molecules into the crystal lattice on the conducting characteristics of the material.

Compound	dc conductivity at 300k (Ωcm) ⁻¹
$\text{Ni}(\text{bqd})_2$	$<9 \times 10^{-9}$
$\text{Ni}(\text{bqd})_2\text{I}_{0.52}\text{S}_b$	$(1.8-11) \times 10^{-6}$
$\text{Pd}(\text{bqd})_2\text{I}_{0.50}\text{S}_c$	$(7.8-810) \times 10^{-5}$
$\text{Ni}(\text{dpg})_2$	$<8 \times 10^{-9}$
$\text{Ni}(\text{dpg})_2\text{I}$	$(2.3-11) \times 10^{-3}$
$\text{Ni}(\text{dpg})_2\text{Br}_{1.0}$	1.8×10^{-3}
$\text{Pd}(\text{dpg})_2$	$<8 \times 10^{-9}$
$\text{Pd}(\text{dpg})_2\text{I}$	$(7.7-47) \times 10^{-5}$
$\text{Pd}(\text{dpg})_2\text{Br}_{1.1}$	$(8.9-13) \times 10^{-5}$

Fig. 3.2 Single crystal electrical conductivities for bis(diphenyl)glyoximates and bis(benzoquinone)dioximates (S_b Solvent is 0.32 toluene, S_c Solvent is 0.52 1,2-dichlorobenzene).

3.1.3 Dihydrodibenzo[b,i][1,4,8,11]tetraazacyclotetradecine complexes

The metallic-like properties of doped conjugated macrocyclic π -electron systems has led to an interest in the class of compounds based upon the dihydrodibenzo[b,i][1,4,8,11]tetraaza cyclotetradecine molecule⁹⁶ (otherwise known as the dibenzotetraaza[14]annulenes). A sizeable range of dibenzotetraaza[14]annulenes has been synthesised (see chapter 3). The redox properties of these molecules are in some ways similar to those of the metallophthalocyanines⁹⁷. Research data indicates⁹⁸ that upon halogenic oxidation the polyhalide species is present in the material as both I_3^- and I_5^- implying only partial oxidation in the complex. Upon substitution of the molecule the general trend is towards a reduction in the conductivity of the material, and this has been associated with a buckling of the molecule that occurs to avoid close intermolecular stacking^{99,100}. Replacement of the metal with H_2 in these type of compounds generally results in large losses in conductivity, a behaviour that differs from the phthalocyanines.

It has been reported that more complex dibenzotetraaza[14]annulenes exhibit high electrical conductivity upon doping with iodine^{101,102}. The synthesis of two particular molecules, namely a dibenzotetraaza[14]annulene derived from 4-dodecylthio-1,2-phenyldiamine and a nickel complex of dibenzotetraaza[14]annulene with tetradecyloxy groups (Fig. 3.3), has allowed the determination and study of the conductivities by the formation of Langmuir-Blodgett films¹⁰³.

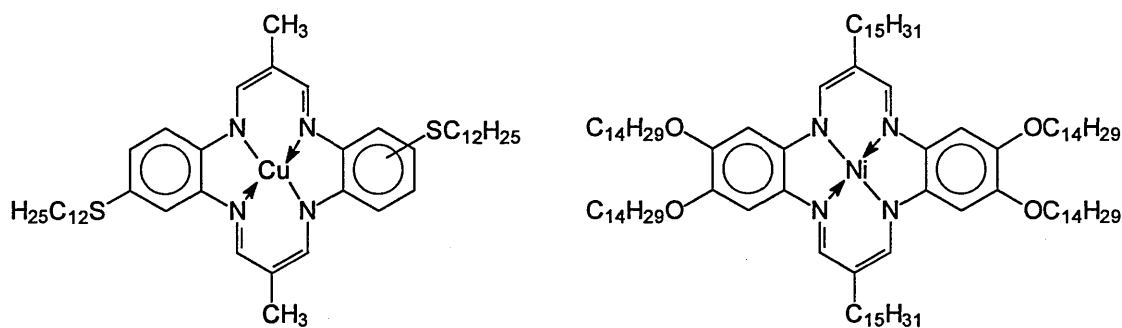


Fig. 3.3 Dibenzotetraaza[14]annulenes used in the formation of Langmuir-Blodgett films.

Results of the study have shown that, as expected, conductivity increases upon halogenic oxidation and that the nature of the oxidant is of prime importance in tailoring the conductivity.

The use of this series of compounds as semiconducting devices has already provided applications as gas sensors that operate by measurement of the fluctuations in dark dc conductivity that occur when an analyte gas (e.g. NO_x) is absorbed at the surface of thin films of copper complexes of the macrocycles¹⁰⁴⁻¹⁰⁶.

3.1.4 Phthalocyanines

Investigations of highly conjugated planar π -electron systems led to an interest in metallophthalocyanines. These metal complexes have readily accessible redox states and demonstrate an increased planar flexibility over the macrocyclic complexes previously discussed. Partial oxidation of these macrocycles (either metallophthalocyanines or the free ligands) with iodine resulted in the formation of a series of molecular conductors¹⁰⁷⁻¹¹¹ that exhibited varied ratios of halogen to phthalocyanine depending on the experimental conditions used in their fabrication.

Efforts to obtain increased understanding of the fundamental properties of such materials has resulted in the synthesis of an extensive class of highly conductive molecular solids that contain stacks of metallophthalocyanine molecules (Fig. 3.4). The molecules were prepared by a procedure which involves iodine oxidation to produce lattices composed of one-dimensional arrays of planar donor molecules (metallophthalocyanine units), with fractionally occupied electronic valence shells and chains of polyiodide counterions. The general structure of such lattices is shown schematically (Fig. 3.4).

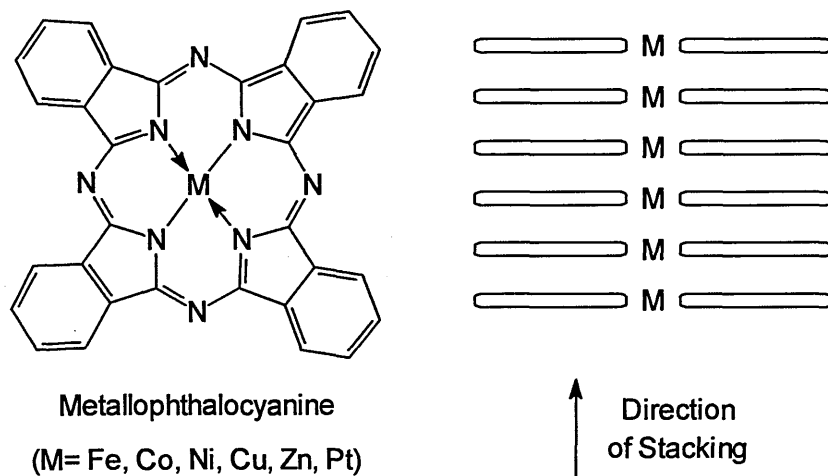


Fig 3.4 The molecular structure of metallophthalocyanine illustrating the crystal structure.

The electrical conductivities of pressed microcrystalline powder samples are comparable to those of other molecular metals, with single crystal conductivities being metallic-like in the metallophthalocyanine stacking direction.

3.1.5 Benzoporphyrinates

The utility of porphyrinic metallomacrocycles¹¹² as building blocks for partially oxidised conducting molecular solids lies in the great scope they offer for modifications in the molecular architecture of both the porphyrin macrocycle and peripheral substituents. Porphyrins closely resemble the phthalocyanines in both structural and electronic aspects and thus are promising materials for new molecular conductors.

The materials are prepared by the reaction of metal-ligand complexes with iodine, and as with other systems previously discussed, partially oxidised complexes result¹¹³⁻¹¹⁶. Analogous to the phthalocyanines, there are two necessary requirements for obtaining high electrical conductivity, which are -

1. The structure should contain infinite stacks of closely packed planar molecules.
2. The occurrence of a partial oxidation of the constituents.

Concordance with these requirements has allowed the synthesis of partial oxidation state crystals through the substoichiometric oxidation of planar metalloporphyrinates.

An example of a study of this type is the preparation and subsequent I_2 oxidation of transition metal complexes of 1,4,5,8,9,12,13,16-octamethyltetraazaporphyrin, $M(OMTBP)$ (Fig.3 5), to form the partially oxidised $M(OMTBP)(I)_x$. Examination of the nickel complex has led to the isolation of conductive single crystals with two distinct degrees of partial oxidation, namely $Ni(OMTBP)(I_3^-)_{0.35}$ and $Ni(OMTBP)(I_3^-)_{0.97}$, both of which exhibit metallic-like conductivity.

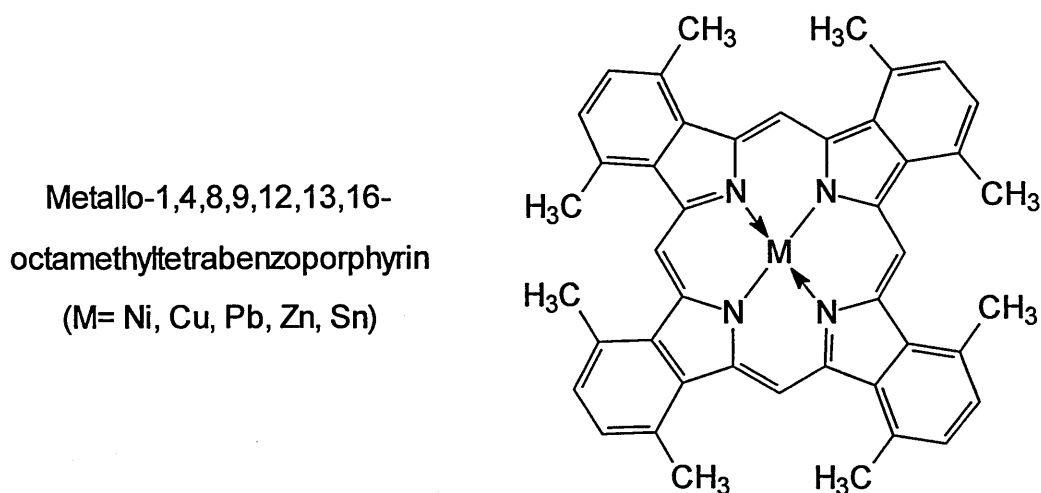


Fig. 3.5 Transition metal complexes of the benzoporphyrinates.

4. Conducting organic polymers

The study of conducting organic polymers gained particular attention following the discovery that polyacetylene could be prepared as thin films having a metallic luster which were able to conduct electricity. The subsequent study of polyacetylene established that the conductivity could be

increased by doping with various electron donating and accepting species to give *p*-type or *n*-type semiconductors⁸¹⁻⁸⁵. Although many other polymers have been researched no other materials have yet been found that exhibit conductivity that approaches that of doped polyacetylene which, as a result, remains the most extensively studied of the conducting organic polymers¹¹⁷.

4.1 Polyacetylene

4.1.1 Synthesis

The synthesis of polyacetylene, like that of many other polymers, is beset by numerous side reactions that occur (e.g. cyclisation, branching, cross-linking). The degree of polymerisation is also variable and many approaches can be used. Initiation of the polymerisation procedure may be carried out by radiation, anionic, cationic and radical procedures.

The preparation of mostly linear, high molecular weight material is best achieved by the use of the catalyst $\text{Ti}(\text{OBu})_4\text{-AlEt}_3$, with control of both the solvent and the temperature¹¹⁸ utilised to achieve the required cis or trans isomer (Fig. 4.1).

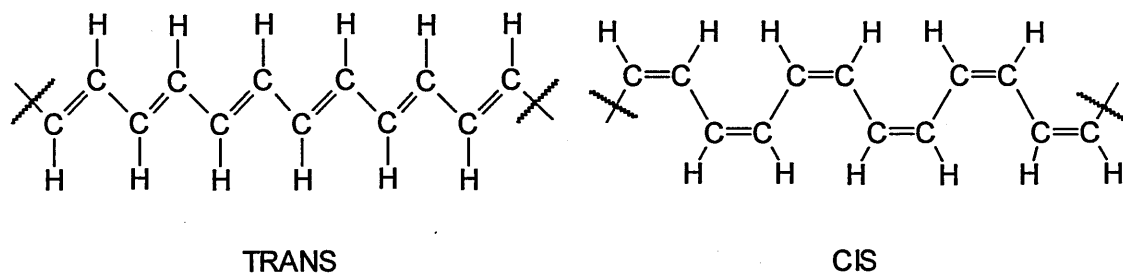


Fig. 4.1 Cis and trans isomers of polyacetylene.

Degrees of polymerisation from 500 to 220,000 have been reported. However, as polyacetylene is insoluble in most solvents, conventional molecular weight studies cannot be employed.

The Durham route for the synthesis of polyacetylene.

A unique approach that overcomes the problems associated with the intractability of polyacetylene is the *Durham route*¹¹⁹⁻¹²¹. Utilising a non-chain scission reaction, the method involves the synthesis of a reasonably stable, tractable precursor polymer that can be purified and fabricated before a thermal conversion to polyacetylene. An example involves the tricyclic monomer illustrated below (Fig. 4.2), which undergoes metathesis polymerisation to give the soluble precursor polymer. Thermal degradation of films of the precursor polymer occurs by an elimination reaction and the resultant loss of a hexafluoroxylylene molecule. The polyacetylene is isolated in a fully dense form.

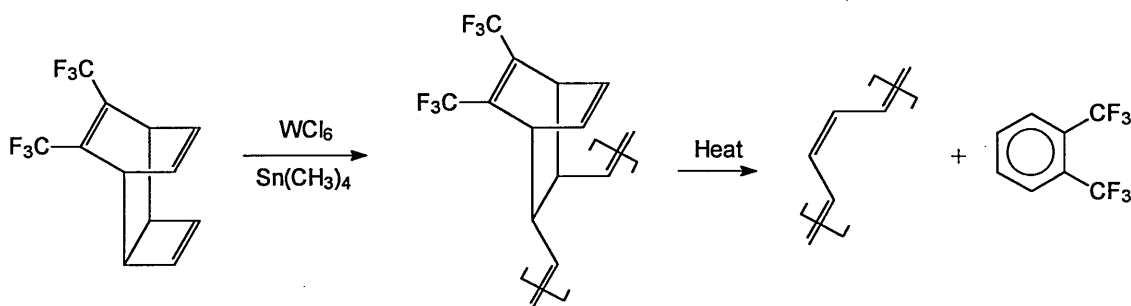


Fig 4.2 Durham route for the synthesis of polyacetylene.

4.1.2 Doping polyacetylene

Pure cis and trans-polyacetylenes have room temperature conductivities of 10^{-10} and 10^{-5} (Ωcm)⁻¹ respectively, but this can be increased by doping with oxidising or reducing agents. Doping can be seen as a charge-transfer process. *P*-type doping is achieved using an electron acceptor such as iodine, where a monovalent anion and stabilised polycarbonium ion are created, conduction in this case involving positive charge carriers. *N*-type doping is achieved with a donor species e.g. Li, and from this a monovalent cation and stabilised polycarbanion are formed. Conversely, conduction in this case involves negative charge carriers.

Several methods are available for the doping of polyacetylene but due to the inherent insolubility of the material in common solvents most methods result in an inhomogeneously doped material. Doping procedures involve the following techniques -

- Doping with gaseous vapours - exposure to AsF_5 , SbF_5 , I_2 or Br_2 .
- Doping with oxidised cations - the use of NO^+ or NO_2^+ ions to produce *p*-type polyacetylene
- Photo-initiated doping - triarylsulphonium salts which decompose under UV to the protonic acid¹¹⁷.
- Solution doping - e.g. *n*-doped polyacetylene produced by the addition of sodium naphthalide in THF.
- Electrical doping - The use of a *cis*-polyacetylene film as the anode in the electrolysis of 0.5M KI solution with the conductivity being monitored during the electrolysis. This method has the advantage of producing both *p* and *n*-type polyacetylene, and it allows the precise control of doping levels.

4.1.3 Derivative polymers of polyacetylene

Derivatisation of polyacetylene has been achieved by the replacement of hydrogen atoms with different pendant groups. This tends to increase the solubility in non-polar solvents whilst retaining the conjugation of the polymer backbone. Examples of the derivatives prepared are shown below (Fig. 4.3).

Poly(phenylacetylene) Poly(propionitrile) Poly(3-chloro-1-propyne) Poly(3,3,3-trifluoro-1-propyne)

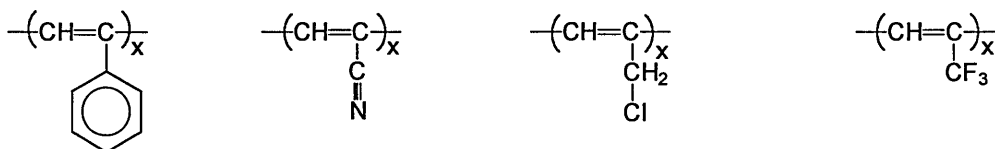


Fig. 4.3 Derivative polymers of polyacetylene.

4.2 Other conducting organic polymers

A number of derivatives of the polyacetylene chain, other organic polymers and their doped derivatives have been prepared and evaluated as conductors. Many of these are based upon aromatic ring systems, such as polypyrrole, polythiophene, poly(p-phenylene) and poly(phenylacetylene) (Fig. 4.4). Unless doped, all of these conjugated polymers remain insulators (with the exception of polyacetylene).

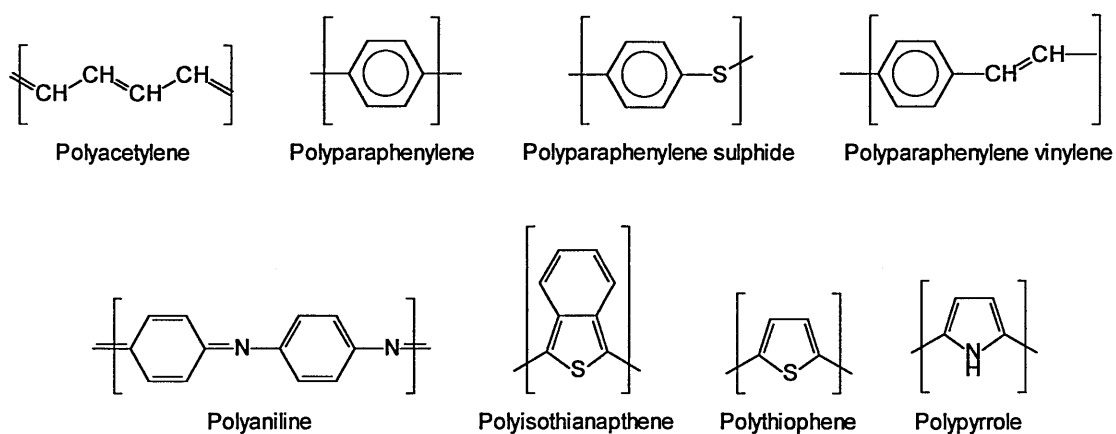


Fig. 4.4 Conducting organic polymers (after doping).

4.2.1 Polypyrrole

Polypyrrole (Fig. 4.5) produces a conductive organic polymer when doped with *p*-type dopants^{122,123}. The electrochemical polymerisation of pyrrole occurs on platinum, carbon or silicon surfaces^{124,125}.

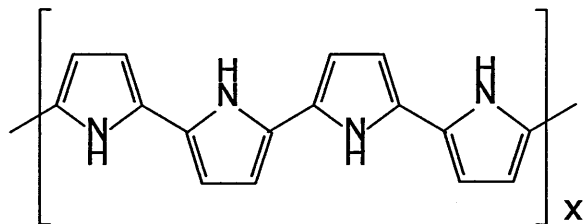


Fig. 4.5 Polypyrrole.

The polymer is believed to form by the linkage of the pyrrole units via the α -carbon atoms, thus keeping the pyrrole rings intact. The pyrrole units can be doped to *p*-type semiconductors by the use of $(\text{Et}_4\text{N})\text{BF}_4$ with the pyrrole units carrying the positive charge which is balanced by the BF_4^- ions.

4.2.2 Polyphenylacetylene

As a derivative of polyacetylene, polyphenylacetylene has a structure where one of the hydrogens on the polyacetylene chains is replaced by a phenyl group. As might be expected the addition of this substituent results in an increase in the solubility of the molecule which is found to dissolve in several nonpolar solvents. Advantages of polyphenylacetylene are thus obvious in respect of methods of study that require a solution of the polymer, for example, doping and processing techniques.

The polymerisation procedure can be achieved by the use of catalysts e.g. WCl_6 , TiCl_4 , with the average molecular weight falling in the range 300 - 15000¹²⁶. Polymerisation solvents and the precise nature of the catalyst have a large influence on the polymer formed¹²⁷. The isomeric configuration of polyphenylacetylene can be controlled by the shrewd control of temperature, solvent and catalyst to produce pure *cis* or *trans* forms as well as the amorphous mixture of the polymer. Extensions to the isomeric forms shown to exist for polyacetylene have been discovered¹²⁸. The *trans* isomer has two forms that are interconvertible by a 180° rotation about the C-C single bond to alter from the *trans transoid* state to the *trans cisoid* (Fig. 4.6). Within the *cis* polymers a sequence of three double bonds in the *cis transoid* state limits the rotation about the C-C bonds, the formation of a helical structure then becomes possible (Fig. 4.7).

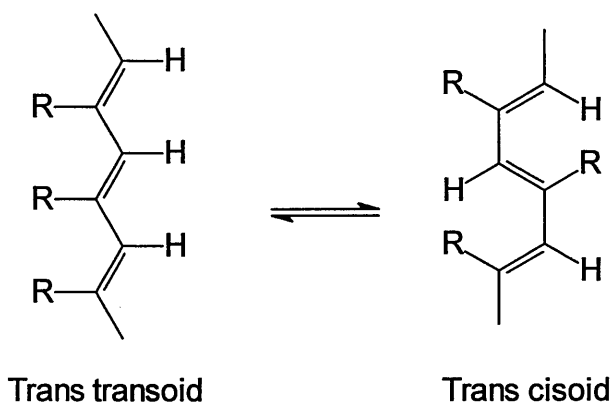


Fig. 4.6 Isomeric states of the trans isomer of polyphenylacetylene (R=Ph).

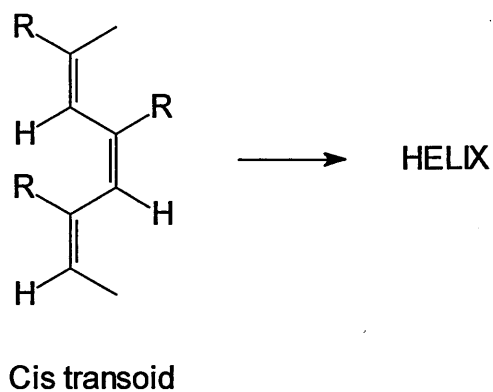


Fig. 4.7 Cis transoid isomeric state leading to helical structure (R=Ph).

4.2.3 Poly(p-phenylene sulphide)

Poly(p-phenylene sulphide) is of great interest due to the unique properties that it exhibits. At present it is the only melt and solution processible polymer that can be doped to produce a conducting polymer. Theoretically it has great value since it is the first polymer that conducts without a continuous system of overlapping C- π orbitals.

Evidence exists¹²⁹ that the doping process with AsF₅ and SbF₅ promotes the formation of C-C links bridging the sulphur linkages to form thiophene rings leading to a system of overlapping orbitals. In these systems, the sulphur atoms contribute to a delocalised electronic structure due to the significant overlap of sulphur p-orbitals and aromatic π -orbitals on the neighbouring rings even where the configurations are non-planar. This illustrates that highly conducting polymers are not restricted to conjugated polymers with extended π systems if the doping process alters the electronic structure.

4.2.4 Poly(p-phenylene)

This polymer is an example of a non-acetylenic, hydrocarbon polymer that can be doped with either electron donors or acceptors to give conducting polymers¹³⁰. The polymer is synthesised by the oxidative cationic polymerisation of benzene using an $\text{AlCl}_3\text{-CuCl}_2$ catalyst at 35°C .

4.2.5 Polyaniline

Polyaniline has been studied for many years and its synthesis has been described in various papers¹³¹⁻¹³³. Recently, a novel synthesis has been described¹³⁴ that involves an oxidation of the monomer to produce the polyaniline. The oxidation of the monomer is carried out in hydrochloric acid (1M) in the presence of ammonium peroxydisulphate, $(\text{NH}_4)_2\text{S}_2\text{O}_8$. The polymer is illustrated below in its various forms (Fig.4 8).

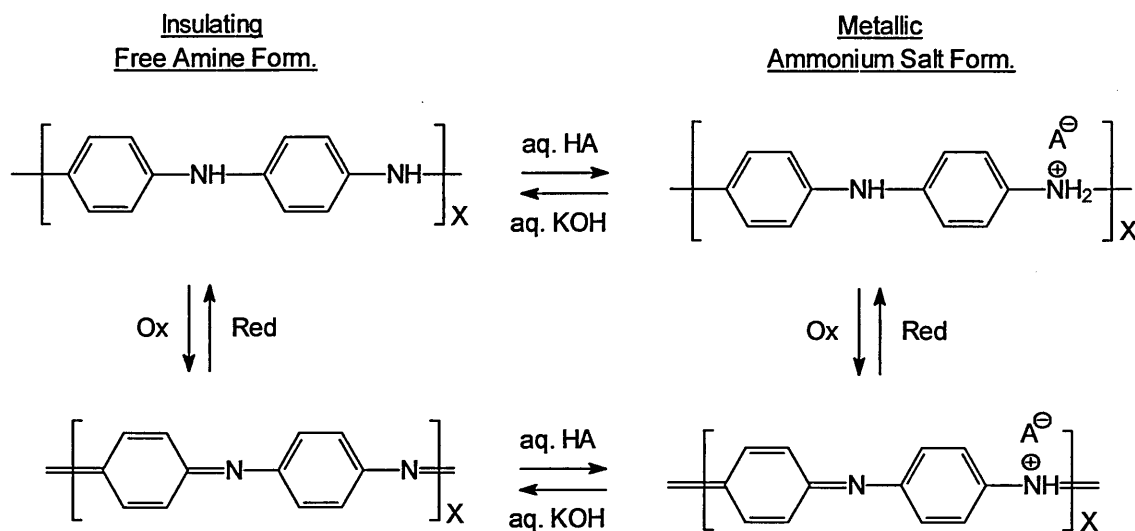


Fig.4 8 Insulating and conducting forms of polyaniline.

4.3 Polymeric compounds and the incorporation of macrocyclic complexes

The incorporation of macrocyclic species into a polymer backbone, either as a main or side chain, is of great interest in the ongoing development of highly conducting materials that are easily processed.

The introduction of conducting macrocyclic species into the polymeric environment serves to introduce an ordered constraint on the macrocyclic units that, as previously discussed, allows orbital overlap of the macrocycle. Even the formation of the polymeric species may serve to increase the conductivity if an extension of the delocalised π -system results as part of the backbone.

Examples of this type include the porphyrin system and range from simple oligomeric systems to extended polymer chains^{103,135} (Fig. 4.9).

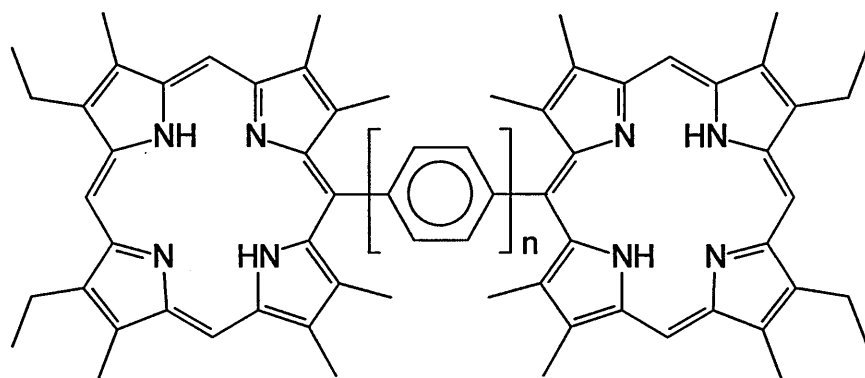


Fig. 4.9 Polymeric and oligomeric macrocyclic polymer systems.

5. Applications of organic conductors

A number of potential applications for organic semiconductors have been suggested, but by far the largest number have been those involving doped polyacetylene polymer systems. Applications include their uses as antistatic coatings, fuel cells catalysts, solar electrical cells, photoelectrodes in photogalvanic cells and lightweight batteries^{136,137}.

The most promising application has been the potential use of polyacetylene as a rechargeable battery. Advances over conventional battery systems have been developed and include lighter, less expensive batteries and improved charging - discharging characteristics¹³⁸.

Chapter 4

Macrocycles and Macrocyclic Complexes

1. Introduction

Since the turn of the century extensive research has been channelled into the study of chelating macrocycles and their complexes. The area of conjugated tetraazamacrocyclic ligands has been one of the chief areas of study since the turn of the century, and their occurrence has been established in heme proteins¹³⁹, chlorophyll and vitamin B12¹⁴⁰. This would suggest that the conjugated macrocyclic ligand is crucial to the multiple roles afforded by the above ligands. The preparation of synthetic analogues of the natural macrocycles has led to a vast array of molecules that have allowed characteristic studies to be made in terms of structure, tautomerism, template effects of co-ordinated metals, synthetic aspects and potential applications. This has led in recent years to an interest in a series of compounds based upon the dibenzotetraaza[14]annulene ring system, the parent macrocycle of the series being illustrated below (Fig. 1.1).

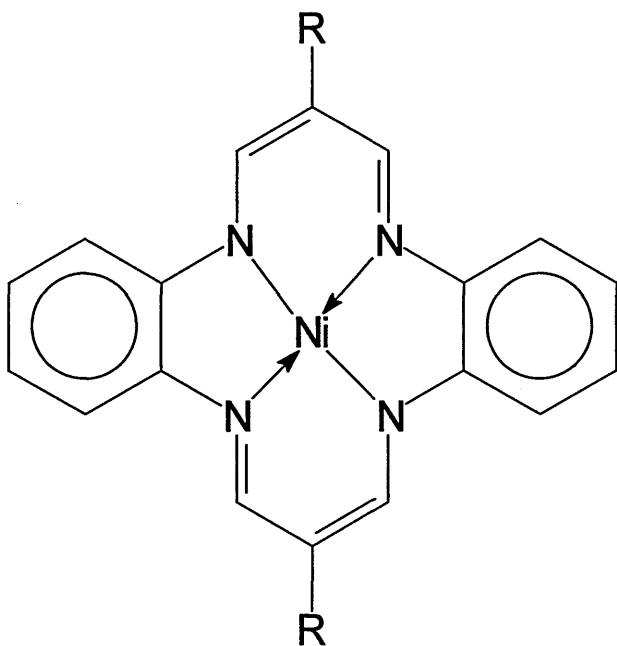


Fig. 1.1 Structure of the parent macrocycle for the Dibenzotetraaza [14]annulene ring system.

2. Phthalocyanines

Prior to the 1960's the number and variety of conjugated tetraazamacrocycles was limited; the biological ring systems previously mentioned were well known but few examples of synthetic macrocycles existed. During this period Linstead was notable for research in the field of phthalocyanines¹⁴¹ and related compounds such as tetraazaporphin¹⁴² and tetracyclohexenatotetraazaporphin¹⁴³(Fig. 2.1).

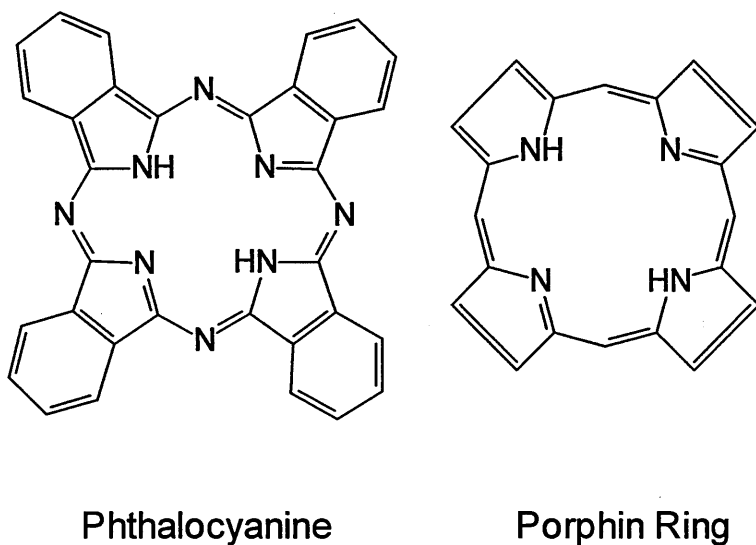


Fig. 2.1 Phthalocyanine and Porphin ring systems.

Due to the complex nature of the structures, the study of natural macrocycles did not provide a simple means of assessing the advantages that this type of macrocyclic structure may offer. For example, the porphyrin ring may provide an aromatic dianion with an extensive π -system, and its reactions with metal ions are complex. Redox interactions are complicated by electron transfers that may involve the metal ion, the ligand, or both. However, it was recognised that synthetic macrocyclic ligands could be used as potential models for studying the behaviour of natural macrocycles and may provide interesting properties in their own right.

3. Historical background to synthetic macrocycles

During the early 1960's a great deal of research was directed towards the synthesis of new macrocyclic ligands that utilised diamines co-ordinated to a transition metal precursor. The reaction between tris-ethylenediaminenickel(II)perchlorate and acetone (Fig. 3.1) was first described by Curtis¹⁴⁴.

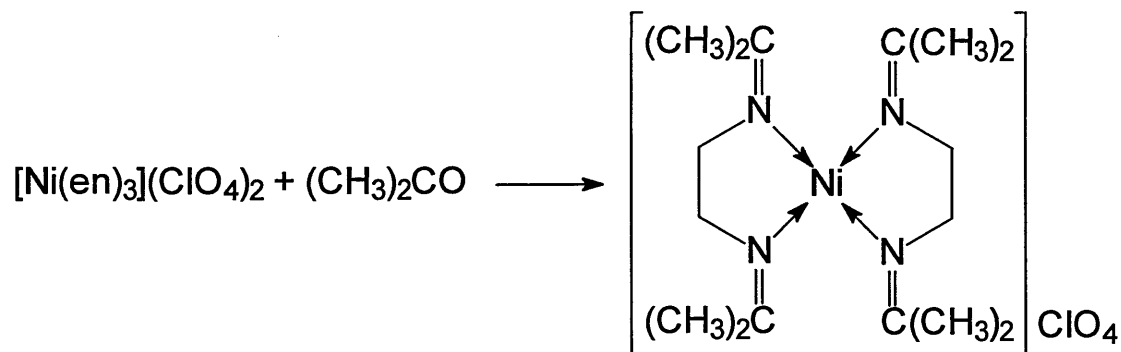


Fig. 3.1 Complex formed from the reaction of tris-ethylenediaminenickel(II)perchlorate and acetone.

Whilst in itself the complex is not macrocyclic, certain analogies could be drawn from the structure that were applicable to the tetraazamacrocycles themselves. Notably the position of the four nitrogens in the square planar configuration directly relates to the square planar metallomacrocycles that were synthesised later. Upon examination of the molecule, steric problems can be isolated due to the planar nature of the azomethine groups $(\text{CH}_3)_2\text{C}=\text{N}-$ coupled with the planarity induced by the nickel complexation. This planar model with standard covalent radii indicates that there would be considerable steric interference between the methyl groups of adjacent isopropylidene units. Skewing of the molecule would introduce distortions which would markedly reduce the stability of the molecule. In fact, π -bonding by the nickel atom using suitably oriented d -orbitals results in resonance involving forms such as that illustrated below (Fig. 3.2).

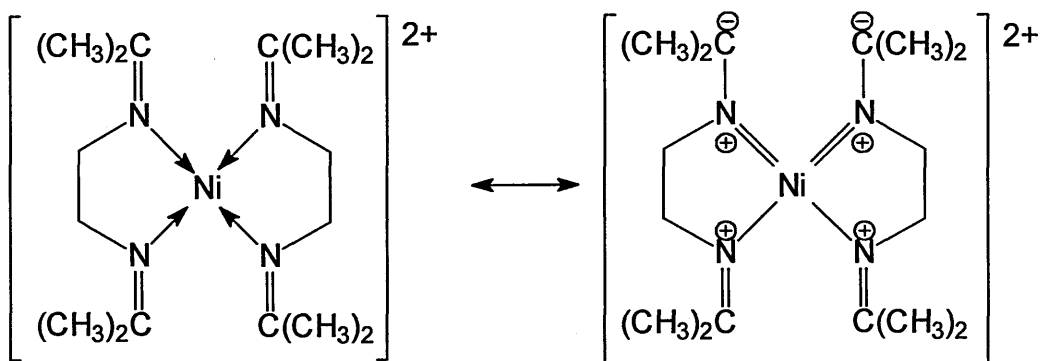


Fig. 3.2 Resonance structures of the nickel(II) complex of the N-Isopropylidene-ethylenediamine Schiff base.

This resonance has two resultant effects, the first effect being an increase in the co-ordinate bond strength. Secondly, due to the reduction in the double bond character of the azomethine groups there is a decrease in the strain associated with the carbon and nitrogen atoms.

The interest in this area was further developed by Thompson and Busch¹⁴⁵ with the development of the reaction illustrated below (Fig. 3.3) leading to the formation of a new macrocycle.

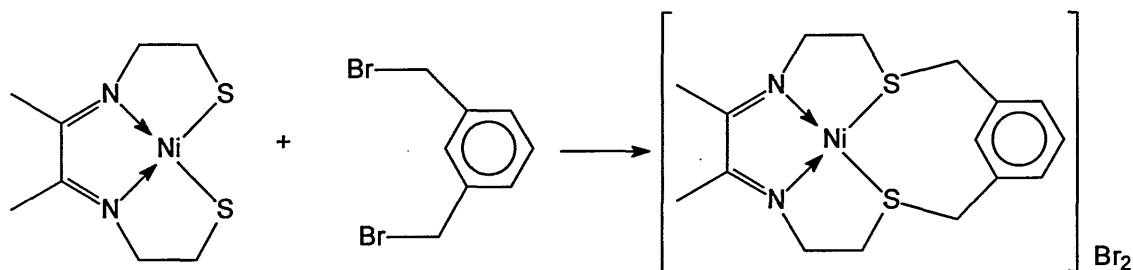


Fig. 3.3 Thompson and Busch macrocycle.

The introduction of new terminology accompanied these developments, most notably the term *template effect*, which reflects the controlling influence of the metal ion in a particular synthesis. Two template effects have been noted; in the *kinetic template effect* the metal ion is utilised to hold the reactive groups in the correct geometry for a selective multistep reaction to occur. The *thermodynamic template effect* involves a perturbation of the existing equilibrium in a system by the metal ion, which has the effect of producing the required product in a high yield as its metal complex.

The synthesis of macrocyclic ligands and their complexes was extended into the area of cyclic polyethers and their metallic complexes in 1967 by Pedersen¹⁴⁶. These so called *crown ethers* (Fig. 3.4) were derived from aromatic vicinal diols that contained from 9 to 60 atoms in the ring (including 3 to 20 oxygen atoms). Many of the cyclic polyethers formed complexes with the cations of salts of the elements belonging to the following groups of the periodic table: all in Ia and Ib; most in IIa; some in IIb; and a few in IIIa, IIIb and IVb. These compounds are salt-polyether complexes formed by ion-dipole interaction between the cation and the basic oxygen atoms symmetrically placed in the polyether ring.

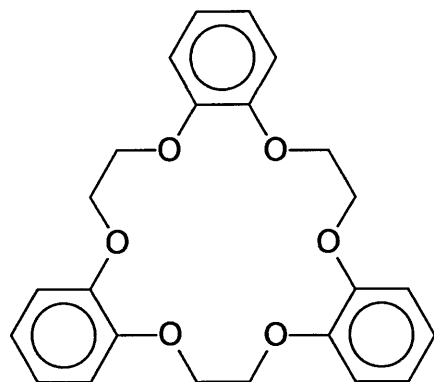


Fig. 3.4 Cyclic polyether.

Conditions necessary for the formation of polyether complexes, and factors affecting their stability include-

- The relative sizes of the ion and of the hole in the polyether ring.
- The number of oxygen atoms in the polyether ring.
- The coplanarity of the oxygen atoms.
- The basicity of the oxygen atoms.
- Steric hindrance in the polyether ring.
- The electrical charge on the ion.

However, the majority of such ligands show a limited tendency to form stable complexes with transition metal ions and are therefore of little use as model systems for natural ligands such as the porphyrins.

In recent years a great deal of research has been directed towards the synthesis of macrocycles containing square planar nitrogen atoms as the co-ordinating species in the macrocyclic framework. Ligands based upon the macrocyclic framework illustrated below (Fig. 3.5) have been prepared¹⁴⁷ and have been found to co-ordinate with chromium(III)¹⁴⁸, iron(III)¹⁴⁹, cobalt(III)¹⁵⁰, rhodium(III)¹⁵¹ and nickel(II)¹⁵².

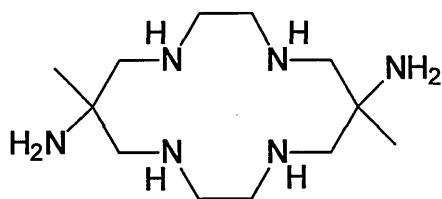


Fig. 3.5 6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine.

However, it has been argued¹⁵³ that saturated tetraazamacrocycles of this type are too flexible to show genuine size match selectivity towards a particular ion and hence the possible applications of any such ligand are certainly limited. An attempt to overcome this problem has involved the synthesis of a variety of reinforced macrocycles¹⁵⁴⁻¹⁵⁷ (Fig. 3.6).

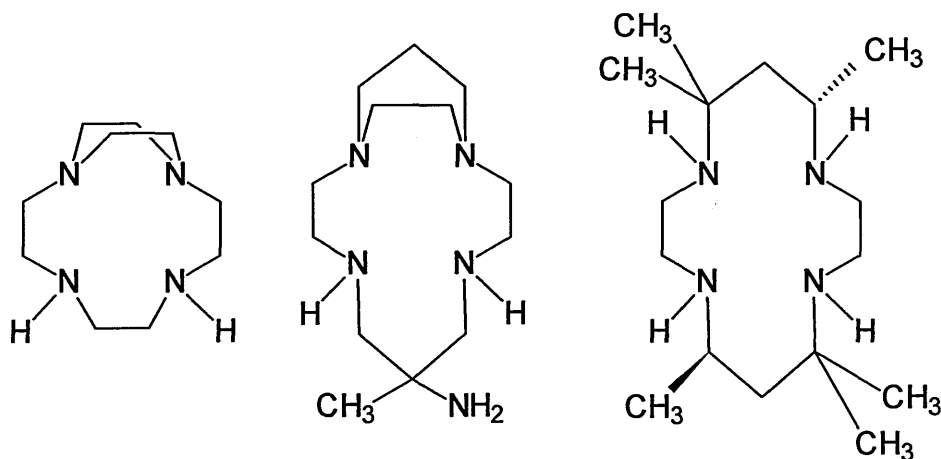


Fig. 3.6 Reinforced macrocycles.

Rigidity in these molecules is induced by cross-bridging or the use of steric influence to induce the square planar nature of the four nitrogen atoms. Selectivity of the molecule towards particular ions is achieved by the control of ring size of the ligand which is also achieved by enforcing rigidity within the molecule.

The synthesis and subsequent polarographic behaviour of similar tetraazamacrocyclic complexes has also been undertaken¹⁵⁸. Basic and reinforced macrocycles were used in the study with the latter being implemented by the use of introduction of steric and multiple bond constraints within the molecule (Fig. 3.7). Variation in ring size of the tetraazamacrocycles was also undertaken to determine ring size effect on the redox properties of the molecule.

The macrocycles¹⁵⁹⁻¹⁶³ themselves have been shown to complex with Cu(II), Ni(II) and Co(III) ions. The subsequent polarographic reduction at a dropping mercury electrode, and the resulting half-wave potentials have been correlated to the ligand field stabilisation and the ring size of the macrocycle. Upon reduction of the copper(II) complexes, waves were obtained that corresponded to a single electron transfer electrode process. Similar one electron transfer waves were obtained in the case of nickel(II) and cobalt(III) complexes.

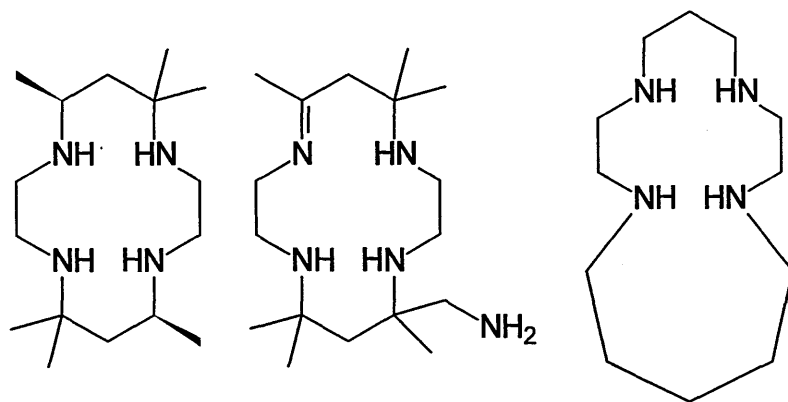


Fig. 3.7 Reinforced macrocycles.

The general reduction process for a copper(II) complex can be represented as¹⁶⁴.



However, only the first reduction of Cu(II) to Cu(I) occurs as the waves are associated with only a single electron transfer process. The half-wave potentials of these complexes show a marked dependence on the macrocyclic ring size and are related to the match between the structural features of the ligand and the stereochemical requirements of the incorporated cation¹⁶⁴. The relative stability of the Cu(II) and Cu(I) states in these complexes is determined by the ability of the ligand to establish strong in-plane interactions. The large ligand field stabilisation effect in such macrocyclic complexes (also termed the macrocyclic effect) makes electron uptake more difficult and limits the reduction to Cu(I).

The synthesis of polyazamacrocycles from so called *crab-like* cyclisation reactions has allowed the preparation of a series of macrocycles with varying ring sizes, that incorporate an amide linkage as part of the ring¹⁶⁵. The reaction sequence uses the combination of a diamine with chloroacetyl chloride to form the starting crab-like bis(α -chloramide) intermediate. These materials resemble a crab with two reactive alkyl chloride groups positioned ready to react with a primary amine or diamine to form a macrocyclic diamide (Fig. 3.8). This diamide may then be reduced to form the polyaza-crown ligands.

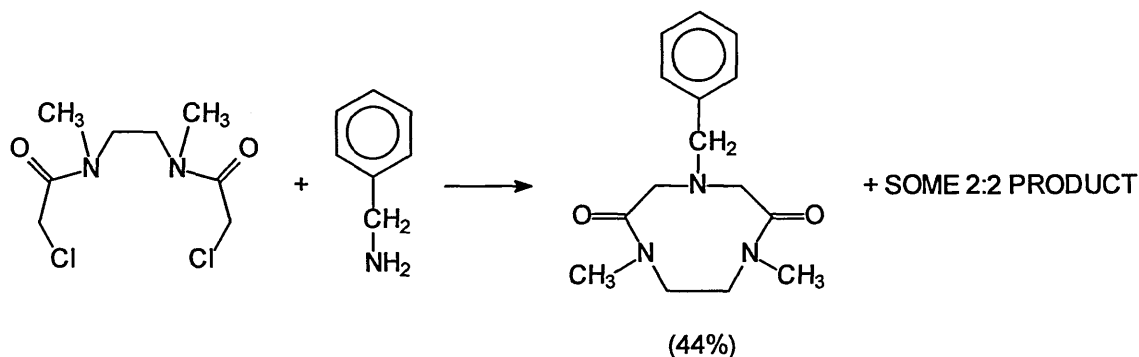


Fig. 3.8 Crab-like cyclisation reaction for the formation of cyclic amides.

The advantages of this cyclisation procedure over similar techniques are-

- The process is a simple one-step procedure from simple starting materials.
- The amide nitrogen is unreactive under the reaction conditions utilised thus eliminating the need for nitrogen protecting agents.
- The process is shorter and the yield is higher than when protecting agents are used.

The intermediate ligands with two amide moieties are useful in their own right as ligands for the complexation of metal ions and the amide containing macrocycles show chelating properties with various metal ions¹⁶⁶⁻¹⁶⁹. A key feature of the macrocycles has been the selectivity exhibited toward particular ions. Upon reduction of the amide functionality with diborane, this selectivity was lost and a broader range of ions were complexed. This may be due to the rigidity enforced by the amide linkage which encourages a molecule with a defined N_4 plane in terms of nitrogen-nitrogen distance and planarity, which therefore limits the size of the ion that can be accommodated.

An interest in the modification of tetraazamacrocycles in terms of symmetry and ligand type has led to several new developments. The introduction of heteroaromatics, not only into the macrocycle itself but as a complexing species has resulted in the preparation of pendant arm macrocycles¹⁷⁰ that incorporate species such as pyridine into their structure (Fig. 3.9).

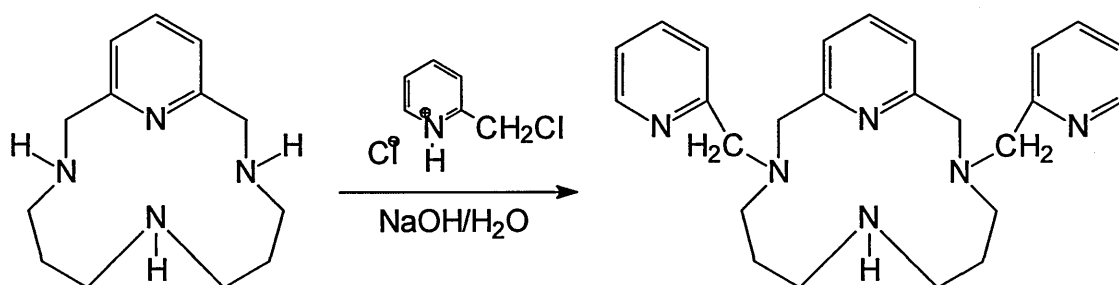


Fig. 3.9 Pendant arm heteroaromatic macrocyclic ligand.

Selective alkylation has enabled the synthesis of macrocycles that contain non-equivalent pendant arms. Preferential alkylation of occurs at the two secondary amine groups flanking the pyridine ring, with little or no attack at the third secondary amine group. This preference is attributed to steric hindrance, the lone pairs of the amine groups flanking the pyridine ring being less hindered by the backbone carbon framework than that of the third secondary amine.

The use of heteroaromatics has been extended into an exciting area of research in which the molecule forms a macrocycle that is incorporated into a polymer backbone to create macrocyclic metal complexes built upon polyethylenimine¹⁷¹. Polyethylenimine and its derivatives have been used as synthetic enzymes¹⁷², since complex formation with substrates and catalytic turnovers of the bound substrates are achieved¹⁷²⁻¹⁷⁶. Polyethylenimine (Fig. 3.10) is obtained by polymerisation of ethyleneimine and therefore contains the ethylamine as the repeat unit. About 25% of the nitrogen atoms of the molecule are primary amines, 50% are secondary amines, and 25% are tertiary amines. The tertiary nitrogen atoms are the branching points on the polymer skeleton. A polycationic microenvironment is provided by the positive charges located on the nitrogen atoms of the polymer backbone, and hydrophobic microenvironment is achieved on the polymer domain by the attachment of alkyl chains to the nitrogen atoms. Some polar organic functional groups are introduced to the polymer by alkylation or acylation of the nitrogens and these behave as catalytic groups.

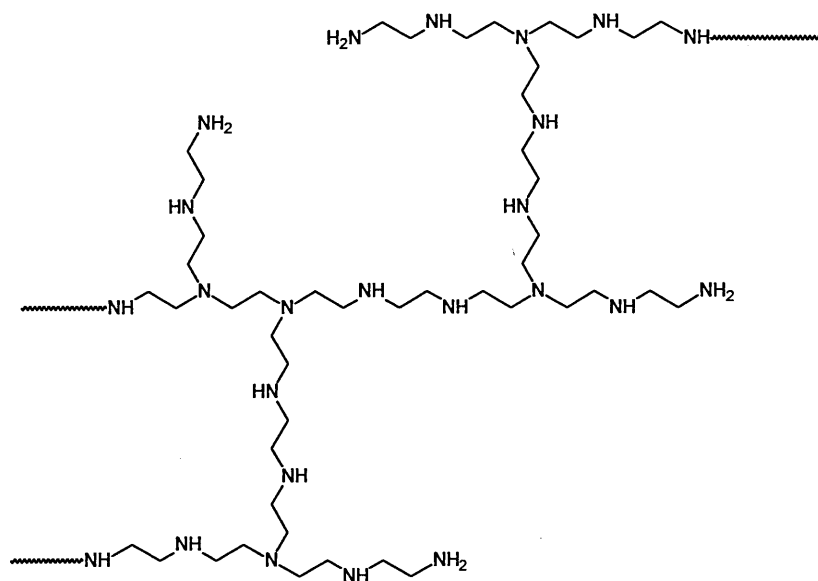


Fig. 3.10 Polyethyleneimine.

Catalytic activity of macrocyclic metal complexes¹⁷⁷ has been intensively investigated. Aldehyde hydration^{178,179}, ester hydrolysis¹⁸⁰, phosphate hydrolysis¹⁸¹ and molecular recognition of small organic molecules¹⁸² are among the reactions in which macrocyclic metal complexes mimic metalloenzymes.

Many of the polyaza metal complexes are prepared by the complexation of carbonyl compounds with polyamines using template procedures¹⁷⁷ as illustrated below (Fig. 3.11).

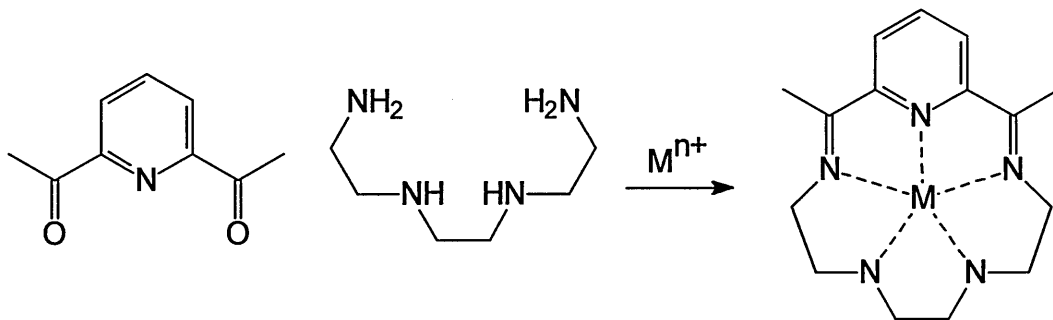


Fig. 3.11 Condensation of dicarbonyl with polyamine to produce macrocyclic complex.

In this regard polyethyleneimine can be regarded as a synthon of the macrocyclic complex as well as the backbone of polymeric macrocycles. This thinking enabled the preparation of polyaza cyclic complexes with polyethyleneimine where the macrocycles existed as domains built on to the polymer backbone (Fig. 3.12).

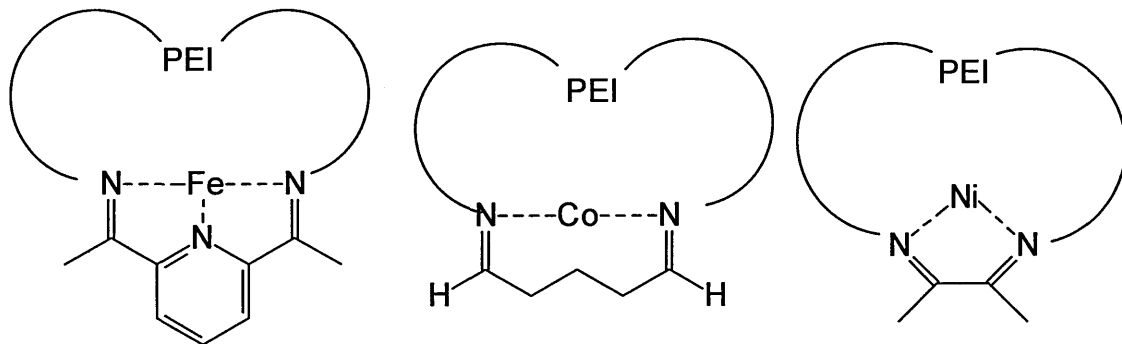


Fig. 3.12 Macrocyclic complexes incorporated into a polymer network.

The use of heteroaromatic units and imine chemistry to create ligand structures that maintain donor atoms in planar configurations around the metal ion has been utilised¹⁸³. Such work represents an important current objective in the study of transition metal systems since, as previously mentioned, these materials can serve as simple models for biological systems. Such complexes are implicated in a number of metal-catalysed enzymatic reactions^{184,185}.

The reaction of 3,4-thiophenedicarboxaldehyde and 1,3-diaminopropane in ethanol gave the tetraazamacrocyclic ligand illustrated below (Fig. 3.10).

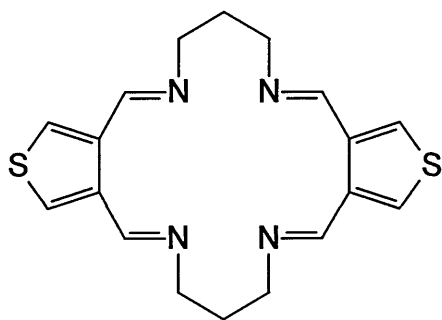


Fig. 3.13 Tetraazamacrocyclic ligand.

Nickel complexes of the molecule have been prepared by both template and non-template procedures and slight modifications have been made to the ring itself to extend the series. The complexes formed can be described as six co-ordinate octahedral structures with two molecules of ethanol as the additional ligands.

The synthesis of macrocyclic rings that contain a mixed donor set¹⁸⁶ as the complexing species has led to the development of macrocyclic complexes that have both the characteristics of the crown ethers and the polyaza macrocycles. The use of macrocyclic ligands in the area of metal-ion discrimination has been the subject of a considerable number of studies¹⁸⁷⁻¹⁹⁰. An example is the use of crown ethers for the selective co-ordination of a number of non-transition metal ions such as individual alkali and alkaline earth metals. The development of macrocyclic systems that selectively discriminate towards particular transition metal ions¹⁹¹ has been approached by placing an emphasis on structural aspects of the molecule which lead to mixed donor macrocyclic ligands (Fig. 3.14).

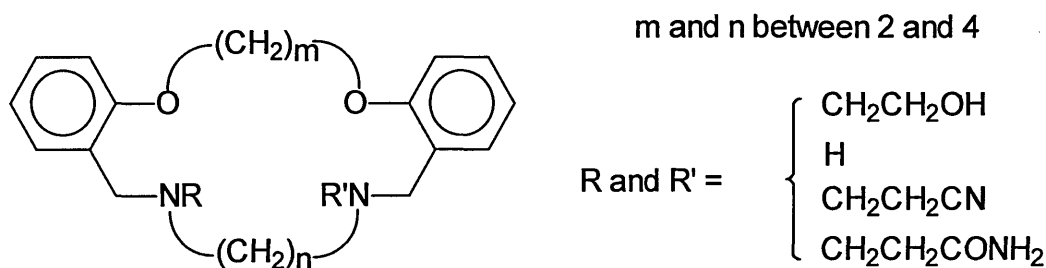


Fig. 3.14 Macrocycle containing mixed donor sets as the ligands.

These macrocycles are structurally intermediate between the cyclic crown ethers and the tetraaza category of macrocycles. Mixed donor macrocycles were employed since they do not usually yield metal complexes with the extreme thermodynamic and kinetic stabilities that are shown by certain complexes of the tetraazamacrocycles^{192,193}.

The preparation of an extensive series of simple tetraazamacrocycles that vary considerably in terms of ring size¹⁹⁴ has been carried out in an attempt to identify any resemblances they may have in relation to the porphyrins. The macrocycles studied (Fig. 3.15). consist of ring sizes of 14, 18, and 22

atoms respectively; this has the obvious effect of increasing the distance between the co-ordinating nitrogen atoms and subsequent differences in complexation arise.

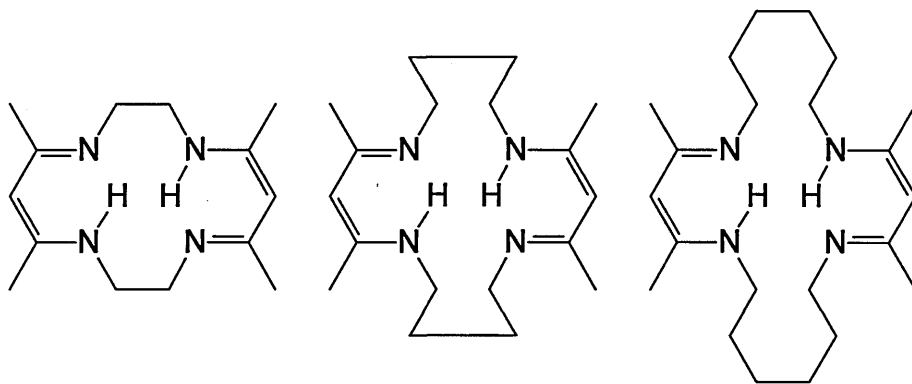


Fig. 3.15 Chemical structure of 14, 18, and 22-membered tetraazamacrocycles.

It was discovered that the 14-membered macrocycle forms mononuclear Cu(II) complexes with a planar structure, whilst the 18-membered macrocycle forms a mononuclear Cu(II) complex with a pseudo tetrahedral structure, and the 22-membered macrocycle forms di- and trinuclear complexes of Cu(II). This suggests that conformational preference of the macrocyclic complex is dependent on ring size.

As indicated in earlier discussions in this chapter, there have been extensive studies into materials that may mimic the characteristics of natural occurring molecules such as porphyrins and important synthetic systems such as the phthalocyanines. An obvious extension of this area of research was the development of materials that contained the naturally occurring materials substituted with the synthetic analogues. The preparation of novel copper phthalocyanine complexes substituted with four 14-membered tetraazamacrocycles¹⁹⁵ has enabled the study of this type of molecule.

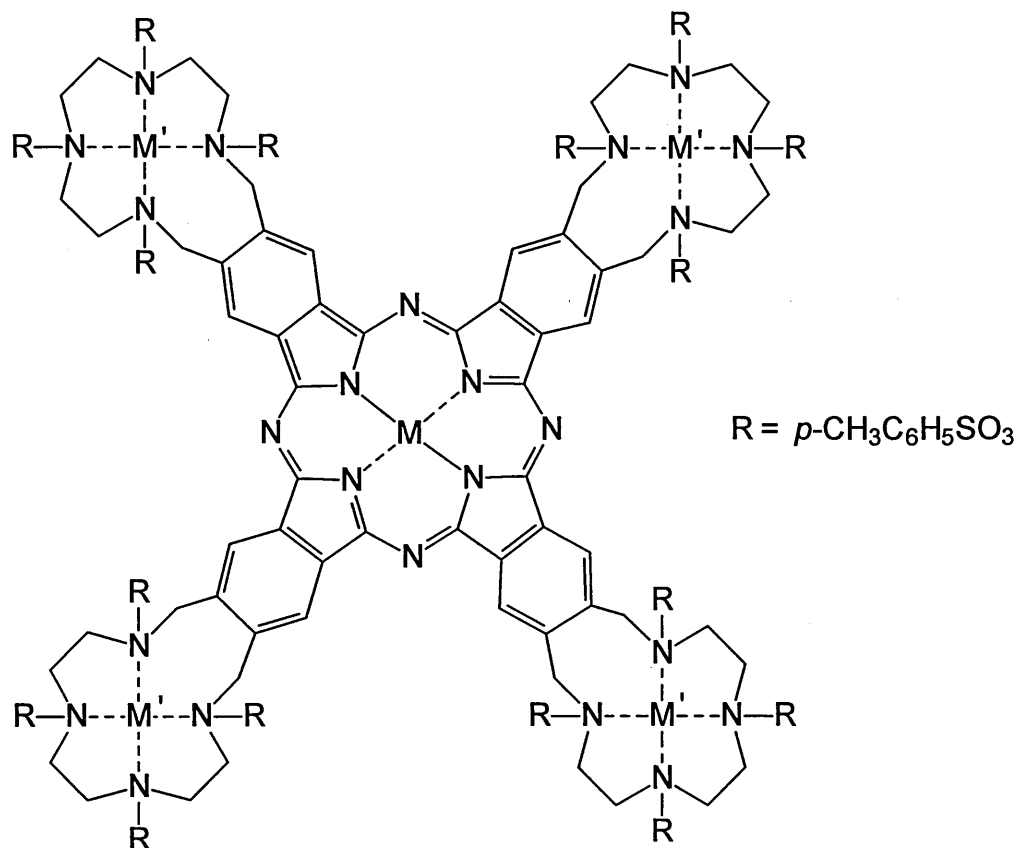


Fig. 3.16 Tetraaza macrocycle substituted phthalocyanine.

The substitution of planar, rigid phthalocyanine cores with flexible chains has been cited as leading to highly ordered systems¹⁹⁶. An example of this type is the substitution of crown ethers onto a phthalocyanine substrate molecule. The molecule then gains the ability to form ion channels allowing the migration of alkali and alkaline-earth cations¹⁹⁷⁻¹⁹⁹. In addition, polyaza macrocycles have recently gained recognition because of the abilities of the polyaza cavity to co-ordinate transition metals²⁰⁰ (Fig. 3.16). Studies of these types of molecule have suggested that a suitable combination of polyaza macrocycle and phthalocyanine may allow new functionalised materials to be prepared which are of importance for both biochemistry and materials science. For example, water soluble pentanuclear complexes of phthalocyanines are relevant as sensitisers in photodynamic cancer therapy²⁰¹ and their symmetry properties can be considered in connection with optical behaviour²⁰². The synthesis of porphyrin analogues has received particular attention due to the potential utility of these compounds in photodynamic tumour therapy²⁰³. A particular area of porphyrin chemistry that has received a great deal of attention has been the formation of a molecule that has thiophene or

furan moieties substituted for some of the pyrrole rings in the porphyrin molecule²⁰⁴⁻²⁰⁶. For example, the synthesis of a difurylporphyrin analog from diformyl difurylmethane and dipyrlylmethane, utilising the Macdonald condensation, has been noted²⁰⁷ (Fig. 3.17).

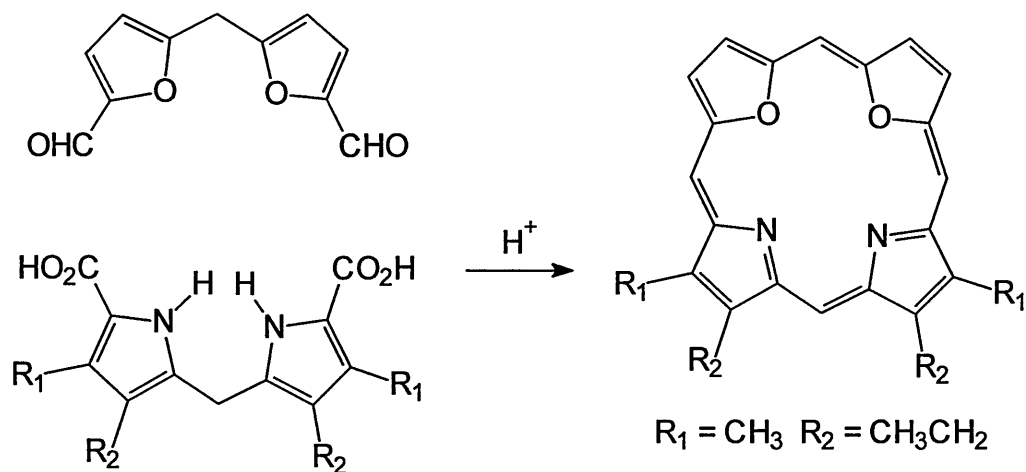


Fig. 3.17 Porphyrin related macrocycle containing furan moieties.

The idea of incorporating synthetic macrocycles into natural systems has been further investigated and the synthesis of the so called quadruply two and three atom, aza bridged, cofacial bis(tetraphenyl porphyrins) (Fig. 3.18) has been developed²⁰⁸. These compounds are related to those in nature that are involved in metabolic processes relating to catalysis by multimetal proteins.

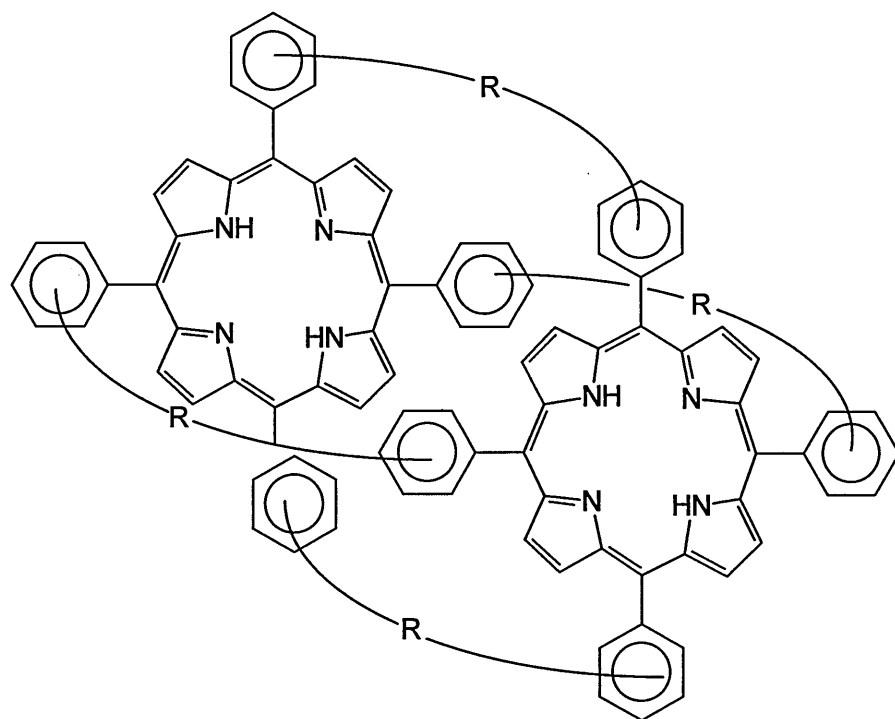


Fig. 3.18 Bridged cofacial porphyrins.

Partially cofacial bis-porphyrins have been used in studies to mimic aspects of energy storage and electron transfer processes that occur in the photosynthetic reaction centre²⁰⁹. The dimers with relatively large cavities have been used as molecular receptors and also as models of π - π aggregation by natural metallated and freebase porphyrins and by metalloporphyrin π -cation radicals.

4. Synthetic macrocyclic tetraaza ligands - The dibenzotetraaza[14]annulenes

Historical studies of synthetic macrocyclic ligands led to the preparation of a series of compounds based upon the non-porphyrin tetraazamacrocycles known as the dibenzotetraaza[14]annulenes. The simplest molecule of this class of compound is illustrated below (Fig. 3.19).

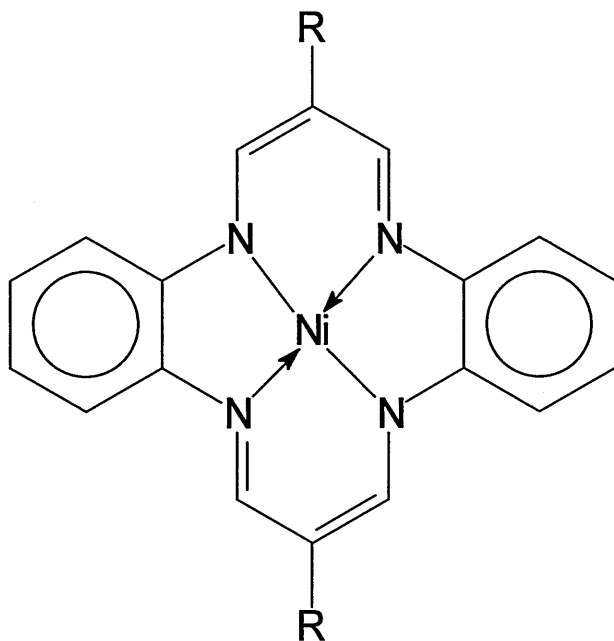


Fig. 3.19 Nickel complex of the parent molecule of the dibenzotetraaza[14]annulene series (R=H).

This family of synthetic macrocyclic ligands shares many common characteristics with the naturally occurring porphyrins, but also features some important differences. Thus, while it is of bio-inorganic interest, it also has many other characteristics which make it of fundamental interest in its own right.

Derivatives of the dibenzotetraaza[14]annulene ring system are of particular interest in a variety of application areas. Thus derivatives with various substituents situated either on the aryl rings or on the propanediiminato bridges have provided metal complexes of interest as toxic gas sensors²¹⁰, electrical conductors²¹¹, electroactive Langmuir-Blodgett films²¹², conductive polymer films and surface modified electrodes²¹³, redox catalysts^{214,215} and as models for natural metallocycle systems such as vitamin B₁₂¹⁴⁰ and heme proteins¹³⁹.

The similarities of the dibenzotetraaza[14]annulenes to the porphyrin ring system are as follows -

- The four nitrogen atoms of the macrocycle are rigidly confined to a plane.
- Upon metal complexation, the ligand usually deprotonates to give a dianion.
- The macrocycles have a conjugated system of double bonds.

However, the differences between the dibenzotetraaza[14]annulenes and naturally occurring systems account for the non-bioinorganic system and hence for the proliferation of new and interesting compounds. The 14-membered ring size of the dibenzotetraaza[14]annulenes compared to the 16-membered ring of the porphyrins favours shorter metal-nitrogen co-ordination bond distances. Secondly, in contrast to the completely delocalised framework of the porphyrins, each of the two negative charges of the dibenzotetraaza[14]annulenes tends to be localised only over the propanediimino bridges that connect the two aryl rings. Lastly, even though the dibenzotetraaza[14]annulenes can be described as conjugated, they would have an anti-aromatic $(4n)$ π system, whereas porphyrins exhibit a $(4n+2)\pi$ electron aromaticity if the conjugation encompasses the whole molecule.

The presence of four nitrogen donor atoms situated in a planar configuration around the metal ion leaves two axial sites on the metal that are available for interaction with substrates. Starting with a few basic macrocyclic frameworks it is considered possible to alter the substituents and degree of saturation within the limits of normal functional group reactivity such that certain properties, for example redox potential, ligand field strength and co-ordination geometry, may approach those found in natural environments. Additionally such manipulations could engender materials with wholly novel properties.

4.1 Synthetic development of the dibenzotetraaza[14]annulenes

Macrocyclic ligands derived from aromatic diamines and β -dicarbonyl compounds via condensation reactions have been prepared using a limited number of synthetic routes. The study of reactions between diamines and β -ketoaminato complexes²¹⁶ of the type illustrated below (Fig. 4.1) has led to the production of dibenzotetraaza[14]annulenes. In this first preparation²¹⁷, the macrocycle was prepared as its nickel(II) complex under severe conditions by reacting the β -ketoaminato complex with molten ortho-phenylenediamine. However, at this early stage of interest in this particular area, problems arose with the condensation of the diamine with the carbonyl of the 3-carbon bridge. These problems were later overcome by the use of suitable substituents at this position.

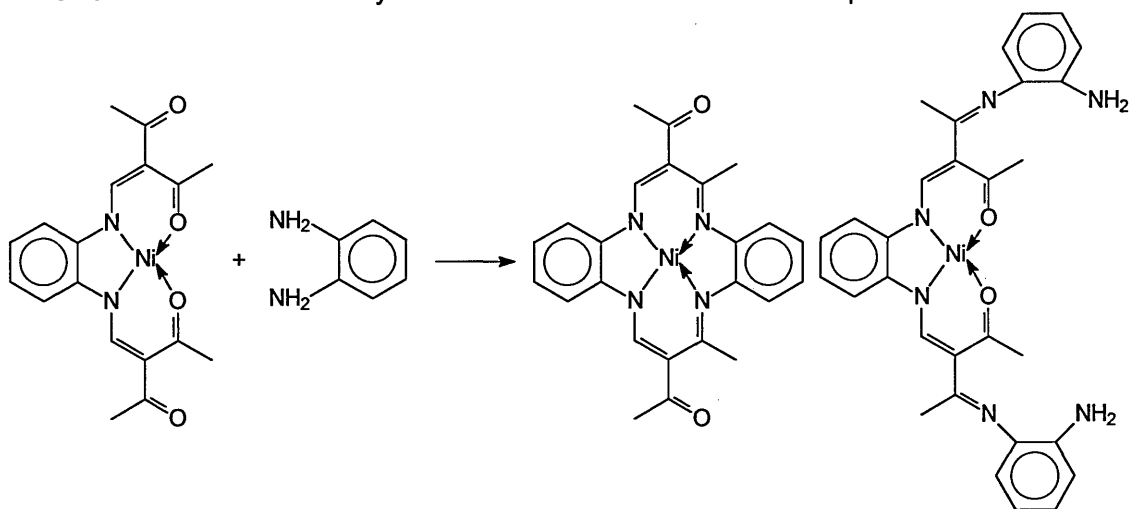


Fig. 4.1 Tetraazamacrocycle formation by the condensation of diamines with β -ketoaminato complexes.

The extension of this type of synthesis and the initial preparation of the parent macrocycle of the series was achieved by Hiller²¹⁸, using a reaction of propargylaldehyde with ortho-phenylenediamine producing yields of up to 27% (Fig. 4.2).

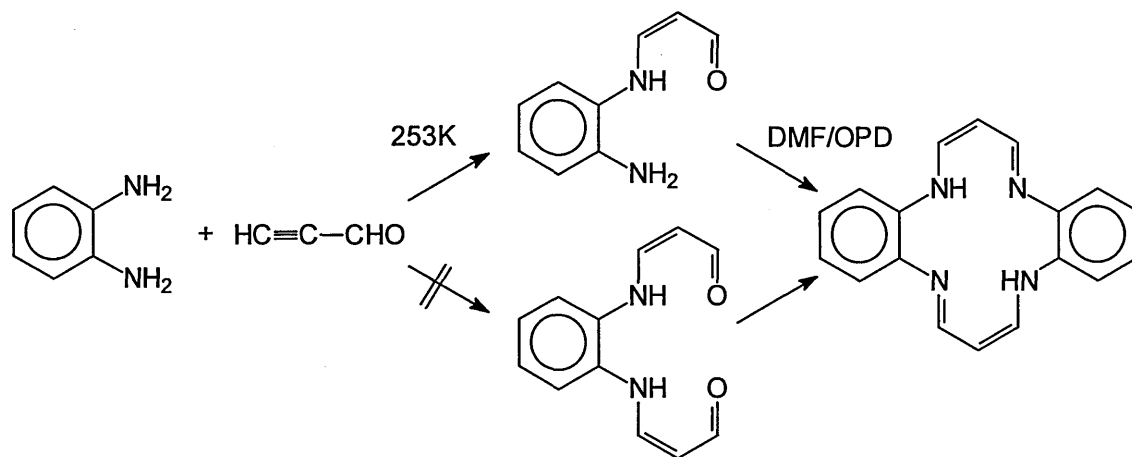


Fig. 4.2 Hiller preparation of the parent molecule in the dibenzotetraaza[14]annulene series.

Subsequent reaction of the ligand with Ni(II) or Cu(II) acetates gave rise to neutral complexes.

However, the same complexes could be prepared directly by the reaction of ortho-phenylenediamine, propargylaldehyde and the appropriate metal salt in dimethylformamide resulting in yields of between 50% and 60%.

During the 1970's the synthetic development of these type of materials was spearheaded by Honeybourne²¹⁹⁻²²² and co-workers. The new procedure involved the introduction of electron withdrawing substituents at the β -position of the diimine bridge by the implementation of substituted malondialdehydes²²³⁻²²⁵. Electron withdrawing groups such as halogens and carbonyls are required to facilitate the formation of the imine linkage between the aldehyde and amine moieties of the reagents by making the aldehyde more susceptible to nucleophilic attack by the nitrogen of the amine. Attempts were made at both template and non-template syntheses of the macrocycle, and as might be expected, higher yields were achieved with the utilisation of template procedures (60% cf. 15-20% for non-template procedures). The normal reaction procedure for the preparation of this type of macrocycle involved stirring the substituted malondialdehyde and ortho-phenylenediamine, with or without a suitable nickel(II) salt in ethanol to produce the free ligand or the hydrated neutral complex (Fig. 4.3).

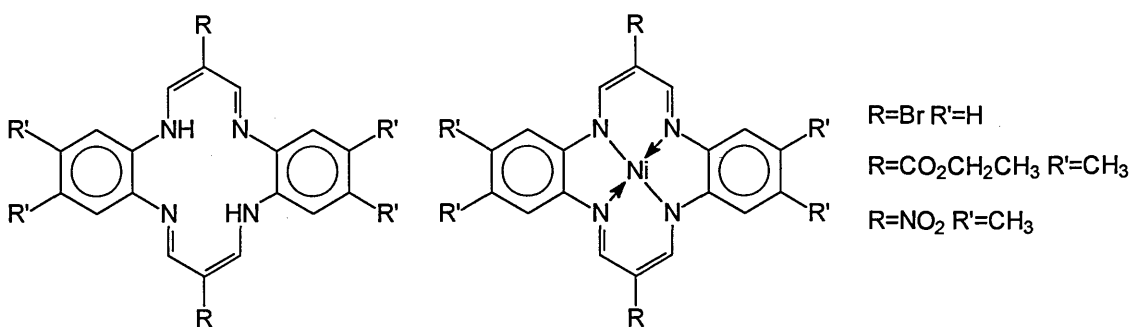


Fig. 4.3 Free ligand and tetraazamacrocyclic complex produced via the Honeybourne procedure.

As might be expected the reaction times for template procedures were very short in comparison to non-template where the reaction times could approach sixty hours. A reduction in the length of time these reactions require can be achieved by the addition of a suitable proton donor. For example, *para*-toluenesulphonic acid or 0.01M acetic acid catalyses the formation of the imine linkage. (Fig. 4.4), thus reducing reaction times.

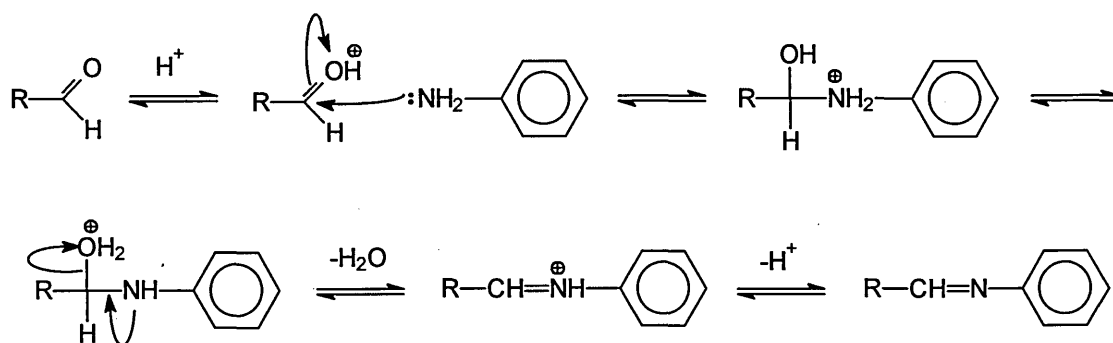


Fig. 4.4 Mechanism for the formation of the imine linkage.

The synthetic procedures for the preparation of dibenzotetraaza[14]annulenes have been developed into other areas by Goedken et al^{226,227}, who used a modification of the Jager procedure²¹⁷. This involved preparation of the macrocycle by a template condensation of *ortho*-phenylene diamine with pentane-2,4-dione in the presence of nickel(II) ions to create the 14-membered macrocyclic ligand illustrated below (Fig. 4.5). Demetallation of the complex with HCl affords the free ligand (Fig. 4.5).

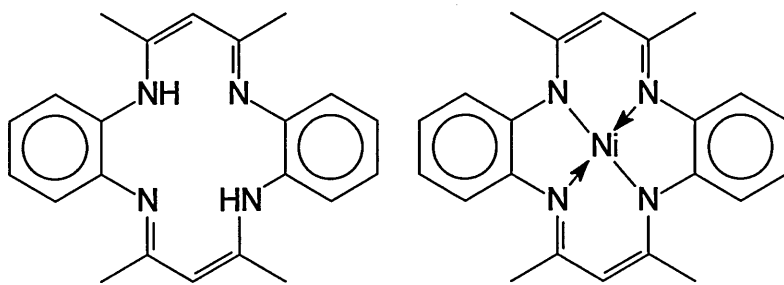


Fig. 4.5 Free ligand and macrocyclic complex prepared via the Goedken procedure.

In an attempt to obtain a better understanding of the binding of small molecules, such as O₂, CO and NO, to iron in biological systems, Goedken then attempted a study of the macrocyclic complex to establish the effect that structural parameters have in influencing the ion reactivity of the ligand²²⁸⁻²³⁰. The complex was first prepared as detailed above and then stripped of nickel(II) with anhydrous HCl in ethanol and isolated as the hydrochloride salt. Neutralisation with base afforded the neutral ligand. Mono(carbon monoxide) complexes of the type [Fe(C₂₂H₂₂N₄)(base)CO], where the base was pyridine, 4-picoline or hydrazine, were prepared by reaction of the free ligand with an anhydrous source of iron(II) usually as the amine complex, under an atmosphere of carbon monoxide.

The formation of these carbon monoxide complexes suggests that co-ordination of mono(carbon monoxide) to iron(II) is not unique to porphyrin type ligands, but is probably a general phenomenon characteristic of a large class of macrocyclic ligands.

Other procedures for the preparation of nickel(II) complexes of substituted dibenzotetraaza[14]annulenes have been reported by Cutler and Dolphin^{231,232}. The first employed the 1,5-benzodiazepinium salt (Fig. 4.6, 1)^{233,234} which in the presence of nickel (II) acetate gave, in either refluxing DMF or methanol, a brown precipitate from which the chelate (Fig. 4.6) was isolated in up to 20% yields. However an alternative in-situ process proved to be more efficient and after refluxing an aqueous solution of ortho-phenylenediamine, 1,1,3,3-tetramethoxypropane and nickel(II) acetate (2:2:1) (Fig. 4.6, 2) an analytically pure chelate was obtained within a three hour period in greater than 85% yield. It should be noted that both procedures entail metal-template mediated mechanisms,

the absence of nickel salts from either reaction resulting in intractable yellow solids devoid of macrocyclic product.

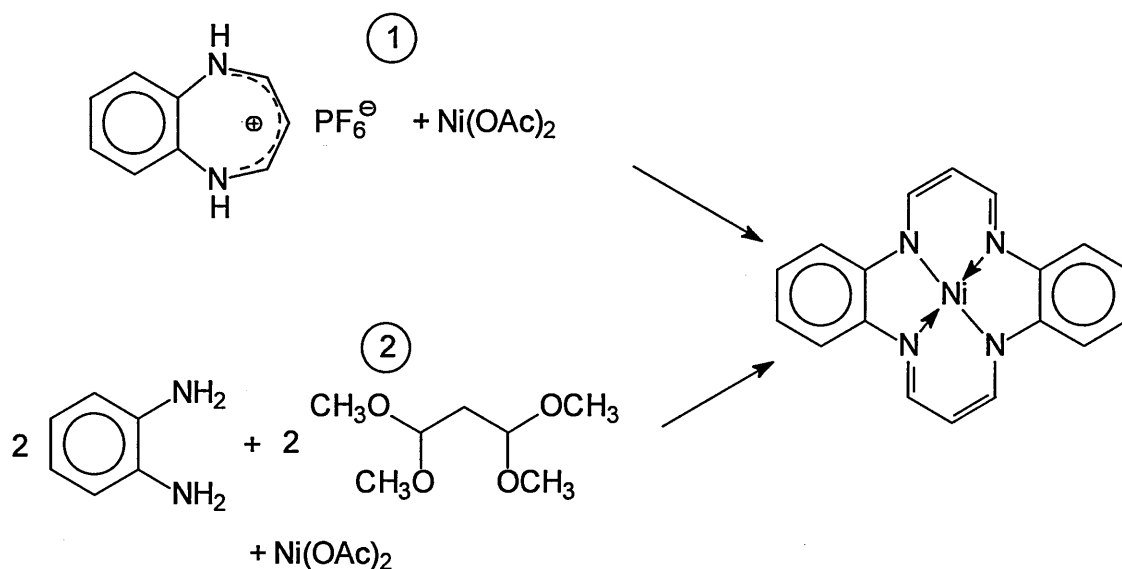


Fig. 4.6 Template synthesis of dibenzotetraaz[14]annulene macrocyclic complexes.

A further source of the diiminato ring, namely substituted acroleins, has been described^{235,236}. The dibenzotetraaza[14]annulene is synthesised from ortho-phenylenediamines and 3,4-dihydro-2H-pyran-5-carbaldehyde as a cyclic 3-alkoxy acrolein.

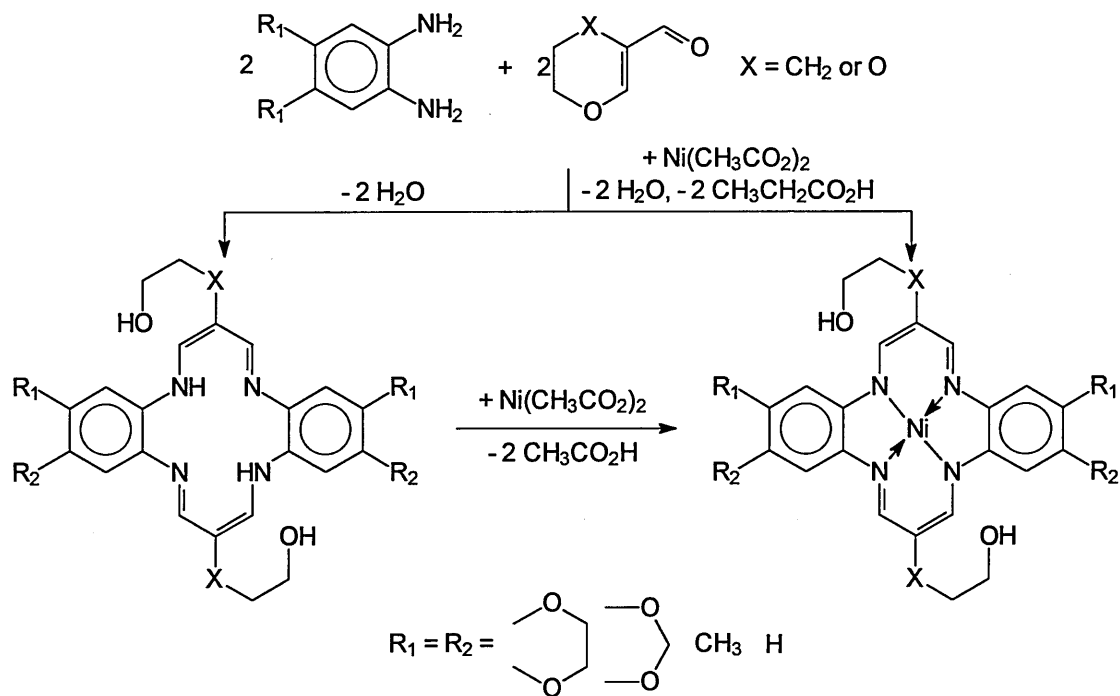


Fig. 4.7 Synthesis of dibenzotetraaza[14]annulenes from substituted acroleins.

The nickel(II) chelates may also be obtained directly by metal template condensation of the aldehyde, the diamine and the nickel salt.

By far the least efficient process for the synthesis of the dibenzotetraaza[14]annulenes is the non-template reaction of ortho-phenylenediamine with β -diketones and β -dialdehydes²³⁷. Yields can be very low and often the reaction products cannot be separated. However, this approach is still pursued since it enables the study of the free ligand when demetallation may be difficult. Undoubtedly polymer formation is a competing process in non-template reactions; however, this may not be a problem, and indeed can be a desirable aspect of some procedures.

4.2 Structure and properties of the dibenzotetraaza[14]annulenes

As already introduced the parent macrocycle for the dibenzotetraaza[14]annulene series is simply 1,4,8,11-dibenzotetraaza[14]annulene (Fig. 4.8), illustrated below.

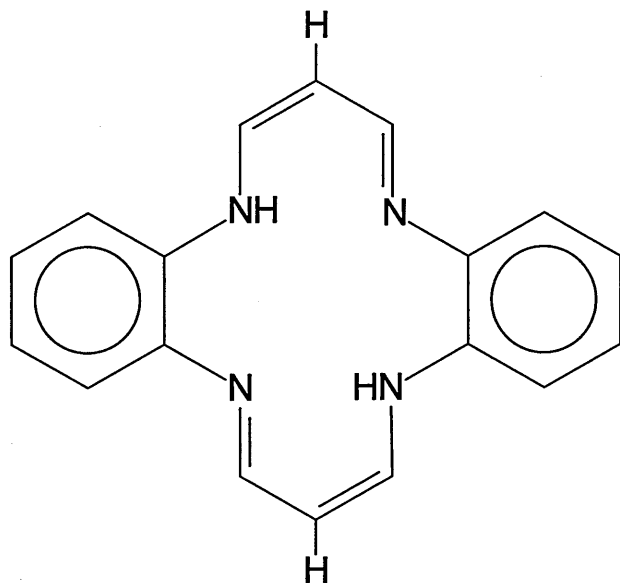


Fig. 4.8 Parent molecule of the 1,4, 8,11-dibenzotetraaza[14]annulene series.

The nickel(II) complex of the molecule is planar and contains delocalised propanediiminato chelate bridges separated from benzenoid rings by single C-N bonds. The molecule may be substituted on the bridges in the R position of the dialdehyde, and in a series of Japanese patent applications over 300 tetraaza[14]annulene compounds were described (Fig. 4.9).

This illustrates the increasingly large number of dibenzotetraaza[14]annulene macrocyclic complexes that has appeared over recent years, and emphasises the versatility of metal ion assisted Schiff base cyclisation reactions. However, limits on the number and type of substituents are imposed since condensation reactions of β -diketones and aromatic diamines in the presence of a metal ion appear to be sensitive to steric effects²³⁸.

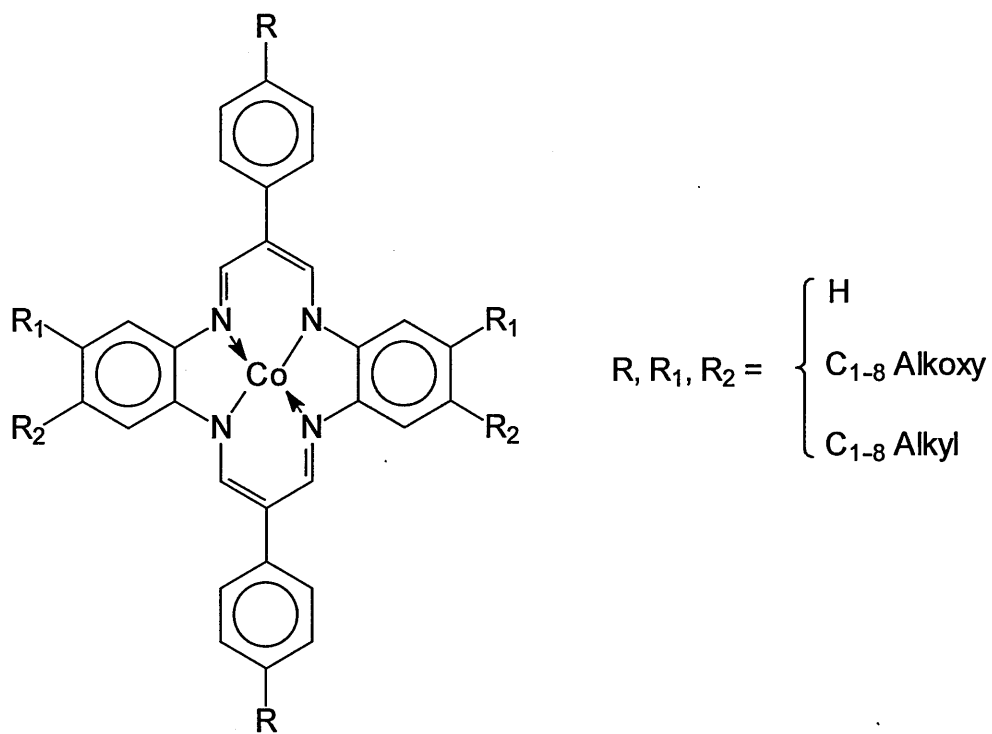


Fig. 4.9 Tetraaza[14]annulenes prepared under Japanese patent.

The tetramethylated Goedken derivative of the parent macrocycle (Fig. 4.5) is, however, different in conformation. Studies of the structure of these molecules by X-ray crystallographic techniques²³⁹⁻²⁴⁵ have shown that the macrocycle and its metal complexes are not planar but are in fact saddle shaped. The adoption of this conformation is due to inherent internal steric constraints resulting from methyl-phenyl repulsions between the side groups and the aryl rings. The enforced saddle shape causes a displacement of any co-ordinated metal from the N_4 plane (Fig. 4.10).

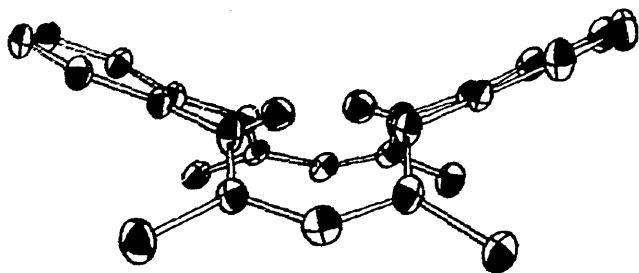


Fig. 4.10 X ray structure showing the saddle deformation of the Goedken macrocycle

The class of dianionic ligands we have been discussing has the systematic name 7,16-dihydrodibenzo[b,i][1,4,8,11]tetraazacyclotetradecine which, for convenience, is often shortened to 1,4,8,11-tetraaza[14]annulene or simply DBTAA.

Unlike the porphyrins and phthalocyanines which satisfy the Hückel $(4n+2)\pi$ electron rule and have aromatic character with extensive double bond delocalisation, the derivatives of the DBTAA series with 16π electrons have nominal antiaromatic character.

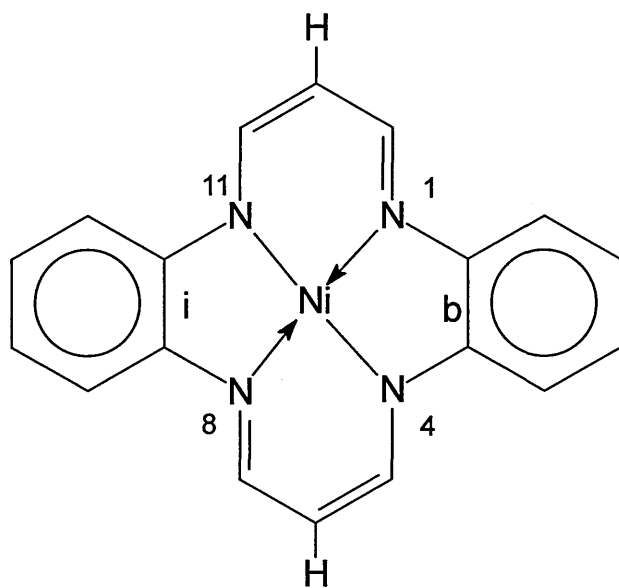


Fig. 4.11 Nickel(II) complex of the parent macrocycle in the DBTAA series.

The nickel(II) complex of the parent macrocycle of the series (Fig. 4.11) is planar and contains delocalised six membered propane-1,3-diiminato chelate rings separated from the benzenoid rings by single C-N bonds, that appear to show little or no preference for π delocalisation²²⁷. By contrast, the tetramethylated lead derivative²²⁶ (Fig. 4.10), adopts a saddle shaped conformation. As previously discussed this is due to interactions between the methyl groups and the adjacent aromatic rings which causes the distortion from planarity (n.b. since the π -system is not delocalised the distortion does not need to affect the electronic structure of the molecule). A consequence of the saddle shape of the molecule is that the ortho-phenylenediamine rings and the diiminate framework are displaced in opposite directions; this has the effect of making the two remaining co-ordination sites chemically

non-equivalent. The single C-N bonds permit a much greater range of torsional motion than is possible for the related porphyrin systems (the extensive double bond delocalisation in the porphyrins impedes any twisting motion about any of the C-N bonds). A large number of derivatives containing various metals, such as Co(II)²¹⁷, Ni(II)²³⁸, Ru(II)²⁴¹, Co(III)²⁴³, Mn(III)²⁴³, Ti(IV)²⁴⁶, Al(III)²⁴⁵, Fe(II)²⁴⁶, Mn(II)²⁴⁷ and Zn(II)²⁴⁷, has been synthesised, and these often exhibit uncommon coordination geometries. In all of these examples, tetramethyl substitution results in a saddle shaped molecule with the metal ion displaced from the N₄ plane. The degree of warping is also strongly influenced by the size of the metal ion²⁴⁸; and it has been shown that there is an ideal ring size for any metal ion having a given metal-donor atom distance. Ring sizes slightly smaller than the best fit show abnormally strong metal-donor bonds as a result of the strain energy being distributed over the whole complex, effectively shortening the metal-donor distance. Similarly, oversized rings result in markedly lower ligand field strengths. For complexes of the DBTAA series (14 membered rings) the best fit is observed for complexes of Co(III)²⁴⁸. Constraints placed on the macrocyclic ring system with respect to expansion and contraction of the N₄ donor core, together with the steric requirements of metal ions with varying radii, often result in unusual co-ordination geometries and uncommon oxidation states²⁴⁰.

4.3 Reactions of the dibenzotetraaza[14]annulenes

The chelate rings in metal acetyl acetonates (pentane-2,4-dionates) and related complexes undergo the reactions that are typical of aromatic systems. The hydrogen at the central position (cf. C-3 of pentane-2,4-dione) of these chelate rings can be substituted with a variety of electrophilic reagents. Halogenation²⁴⁹ and nitration²⁵⁰ reactions have been effected in this system with no rupture of the chelate ring. As stated previously, the diiminato chelate rings of the DBTAA complexes are similar to those of metal acetyl acetonates and have been found to react with various acyl chlorides²⁵¹ (Fig. 4.12). The products were formulated as the hydrochloride salts and were sensitive to moisture, in some extreme cases reverting to the starting materials.

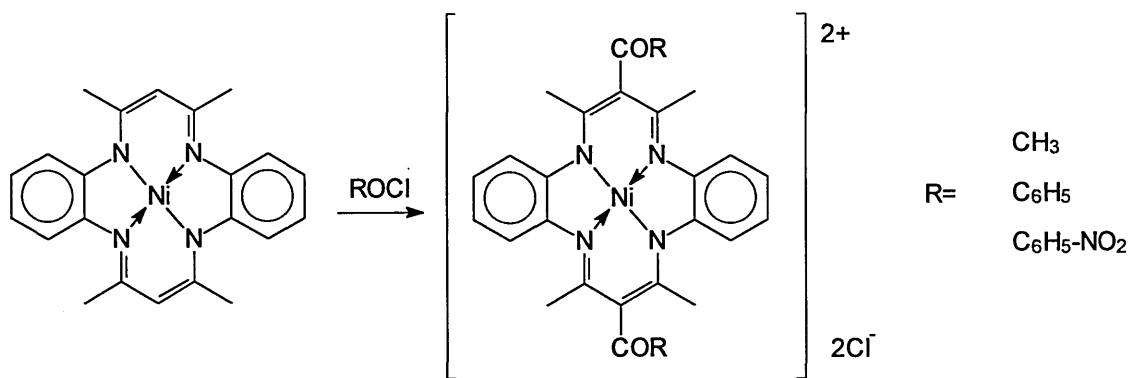
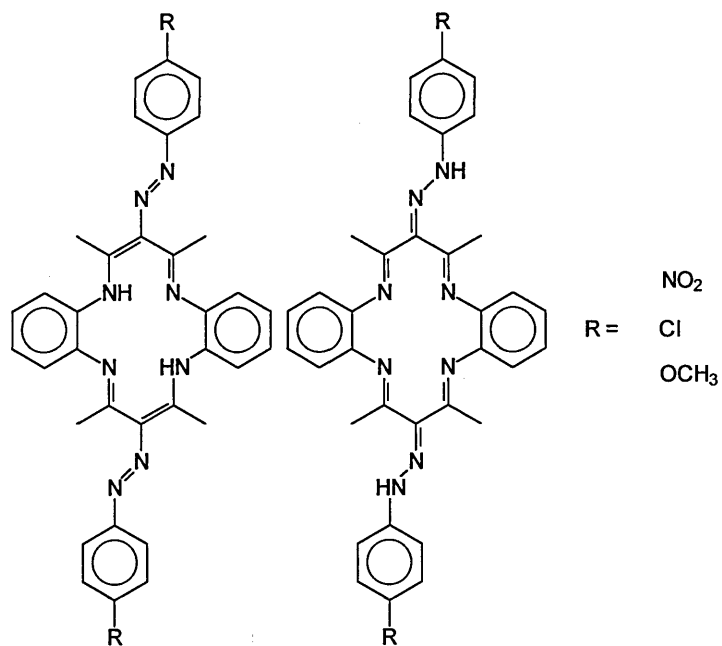


Fig. 4.12 Reaction of the DBTAA series with acyl chlorides.

Tetramethyl substituted DBTAA is known to react with diazonium salts to give bis-azo macrocyclic ligands (Fig. 4.13 a)²⁵²⁻²⁵⁴. The ligand undergoes tautomerism to give the hydrazone (Fig. 4.13 b), but complexation to a metal ion at this stage results in the reformation of the bis-azo structure.



Figs. 4.13 a and 4.13 b Diazonium and hydrazone derivative obtained from the tetramethylated DBTAA.

The reaction of the cobalt(II) complex of the tetramethylated DBTAA with oxygen has been described²⁵⁵ with extremely interesting results (Fig. 4.14). The oxidation reaction resulted in the formation of a Co(III) complex, in which one of the 2,4–propanediiminato bridges is converted into a β -imine donor function with an adjacent α,β -unsaturated carbonyl.

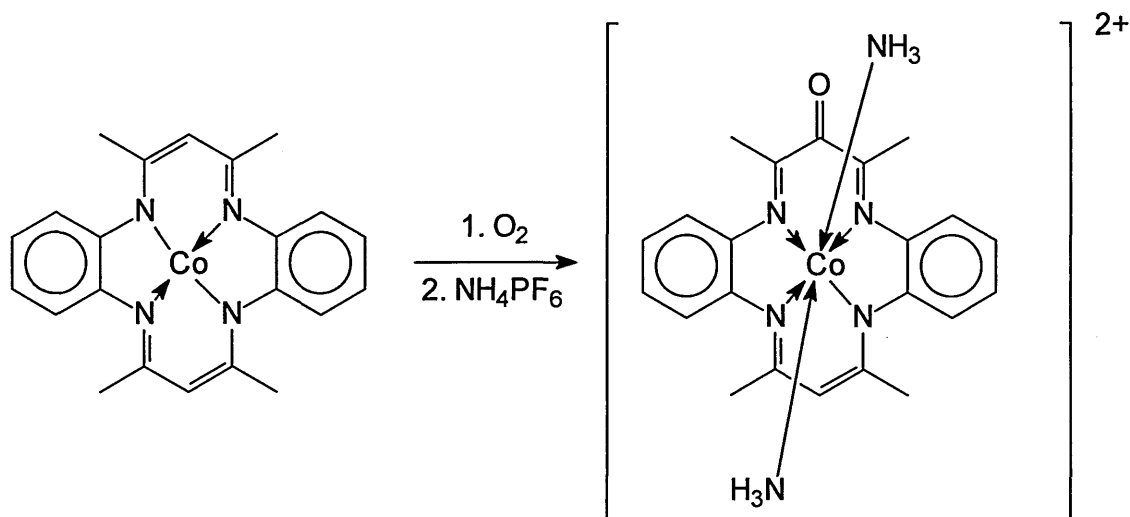


Fig. 4.14 Oxidation of the Co(III) tetramethylated DBTAA complex.

4.4 Applications of the dibenzotetraaza[14]annulenes

Although the initial impetus for research into the dibenzotetraaza[14]annulenes was drawn from the desire to create synthetic mimics of naturally occurring biological systems such as the porphyrins and phthalocyanines, the DBTAA series has also received the attention of researchers in several other areas, particularly for their potential use as catalysts^{213,256} and as precursors for electrically conductive polymers^{210,211,237,258}. Honeybourne²⁵⁹ has reported that thin films of complexes of the DBTAA series exhibit increases in conductance when they are exposed to environmentally deleterious and toxic mixtures of NO_x gases, and that the magnitude and reversibility of the response is dependent on both the concentration of the NO_x gases and the nature of the peripheral substituents of the macrocycle. Films of these macrocyclic compounds coated on non-conducting supports have been examined as toxic gas sensors^{260,261} based on the surface dark d.c conductivity changes.

Bereman et al²¹³ have described a series of surface modified electrodes based on the oxidative electropolymerisation of the monomeric complexes Ni[Me₄(RBzo₂)[14]tetraene N₄], (R= CH₃, H, Cl, NO₂, CO₂CH₃). Repetitive scanning in the oxidative region during cyclic voltammetric measurements on the complexes resulted in the growth of reproducible films on the electrode surface which remained electroactive. Oxidation results in the formation of a dimeric compound composed of two macrocyclic units joined via a carbon-carbon single bond bridge in a manner similar to that found in the formation of binuclear complexes (Fig. 4.15), reported by Dabrowiak²⁶².

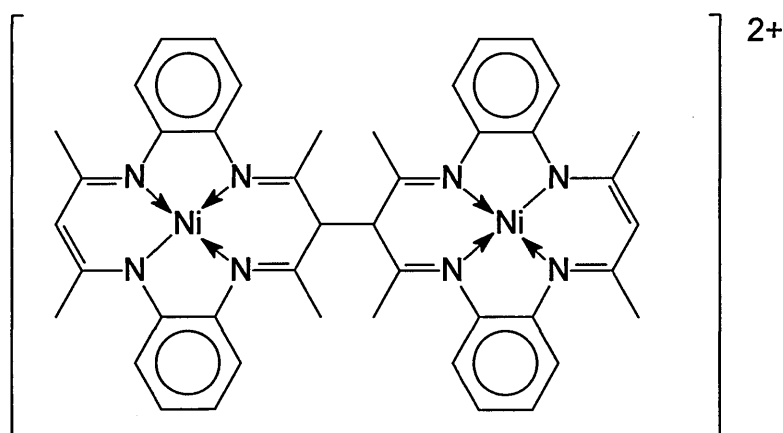


Fig. 4.15 Dimeric macrocyclic compound.

4.5 Unsymmetrical macrocycles based upon the dibenzotetraaza[14]annulenes

The present investigation into the DBTAA series is aimed at the development of syntheses of new macrocycles related to those discussed previously, but where the target molecules are unsymmetrically substituted (Fig. 4.16).

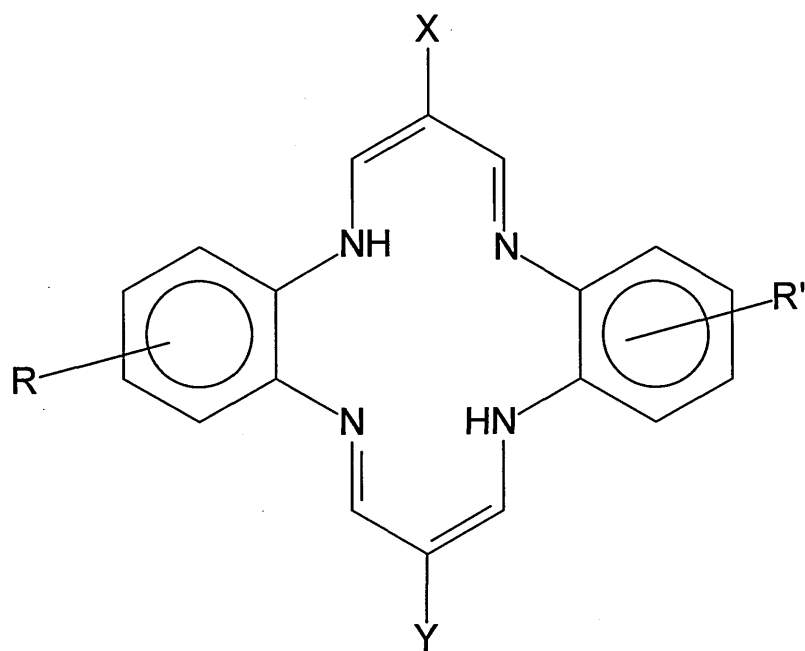


Fig. 4.16 Unsymmetrical macrocycle

Although the attempted modelling of biological systems appears to be possible by implementation of the DBTAA series, there is an inherent problem with the molecules so far discussed in that their potential applications are limited by their symmetrical nature. Symmetry has two major effects on the properties of these molecules; firstly, solubility of the molecule is poor due to the lack of interaction between the solvent molecules and the macrocycles themselves. Secondly, the potential applications of these molecules in the areas of semiconduction and liquid crystals depend upon the ability of the molecules to pack closely together in an ordered microcrystalline environment. For this to occur the macrocycles must have the correct molecular shape and have a dipole moment which allows the molecules to align in an ordered configuration - essentially there is a requirement for an unsymmetrical macrocycle. It is proposed that the introduction of these key features into new macrocycles may provide improved structures with regard to applications in the broad areas of coordination chemistry and molecular electronics²⁶³.

The macrocyclic Schiff base ligand is most commonly synthesised as its metal complex in a one step procedure leading to a symmetrical complex (Fig. 4.17).

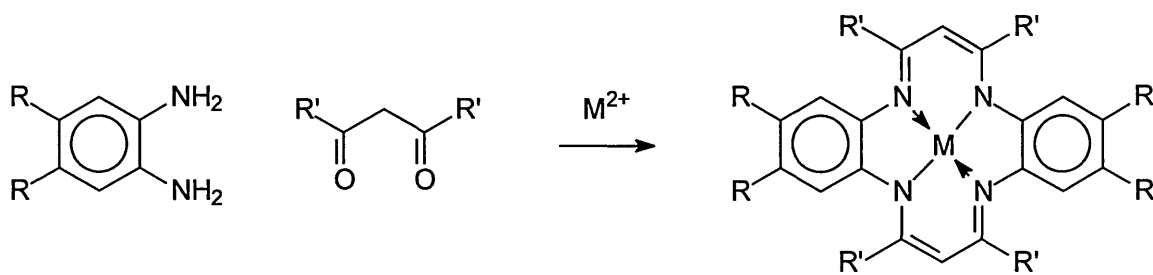


Fig. 4.17 Synthetic procedure for symmetrical macrocyclic complexes.

The metal ion may be envisaged as acting as a thermodynamic template producing the required product, often in high yield, as its metal complex. Non-template synthesis of macrocyclic imine ligands is less favoured and lower yields are obtained.

The conventional procedures offer poor synthetic routes to the target DBTAA's with major problems arising from the number of possible by-products that may occur if procedures similar to that discussed previously are followed (Fig. 4.18), e.g. consider the condensation of two different diamines with two different dicarbonyl compounds.

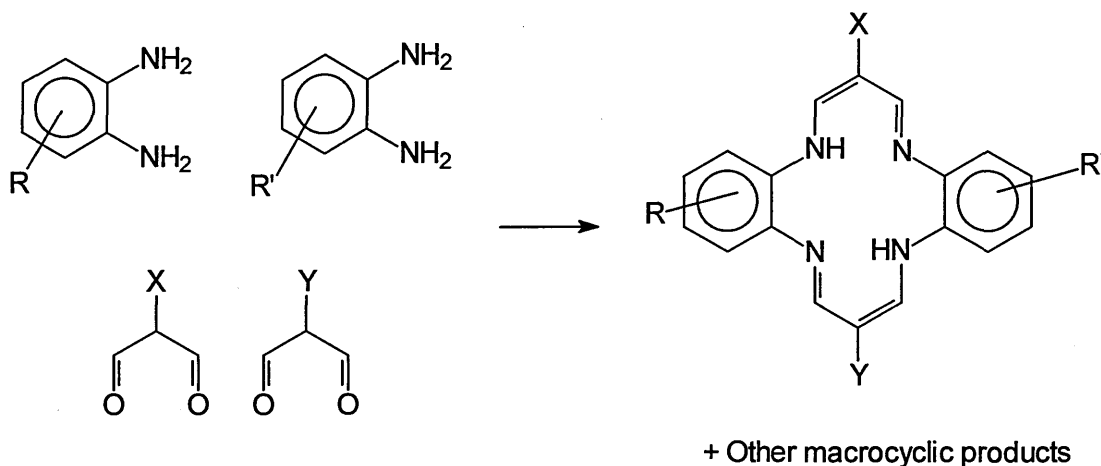


Fig. 4.18 Adoption of the symmetrical scheme for the preparation of unsymmetrical macrocycles may lead to problems!!

The extensive side reactions lead to the formation of 1,5-benzodiazepines, which themselves are formed by the condensation of ortho-phenylenediamines with β -dicarbonyls^{264,265}, benzimidazoles and linear or branched chain polymeric material (Fig. 4.19).

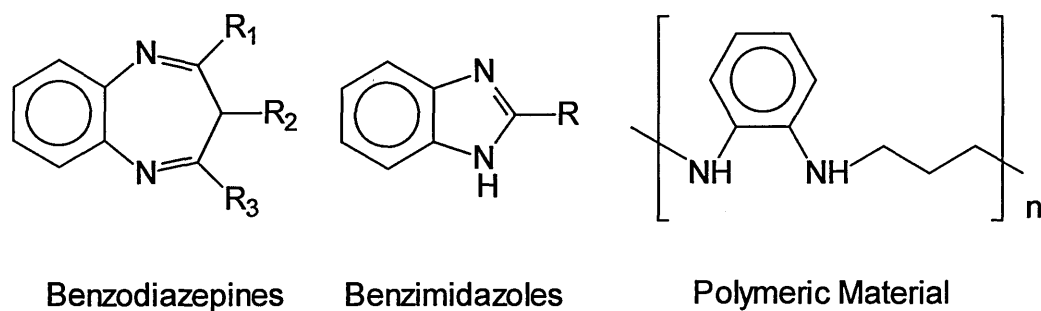


Fig. 4.19 Side products from the attempted simple preparation of unsymmetrical DBTAA's.

However, one procedure reported by Cutler, Dolphin and Alleyne²³² does allow the preparation of macrocycles that exhibit non-symmetrical features through one of the molecular planes. The procedure involves the hydrolytic ring opening of a 1,5-benzodiazepinium salt²⁶⁶⁻²⁶⁸ to the corresponding monoanil, or the more usual ortho-phenylenediamine and β -dicarbonyl, but the significant point is that the procedure allows the isolation of an uncyclised nickel(II) chelate which may then undergo further reaction to yield the unsymmetrical macrocycle (Fig. 4.20). The isolation of the uncyclised nickel(II) chelate is achieved by the addition of an excess of ammonium hexafluorophosphate which then allows the purification of the salt from an acetone-ether solution in high yield.

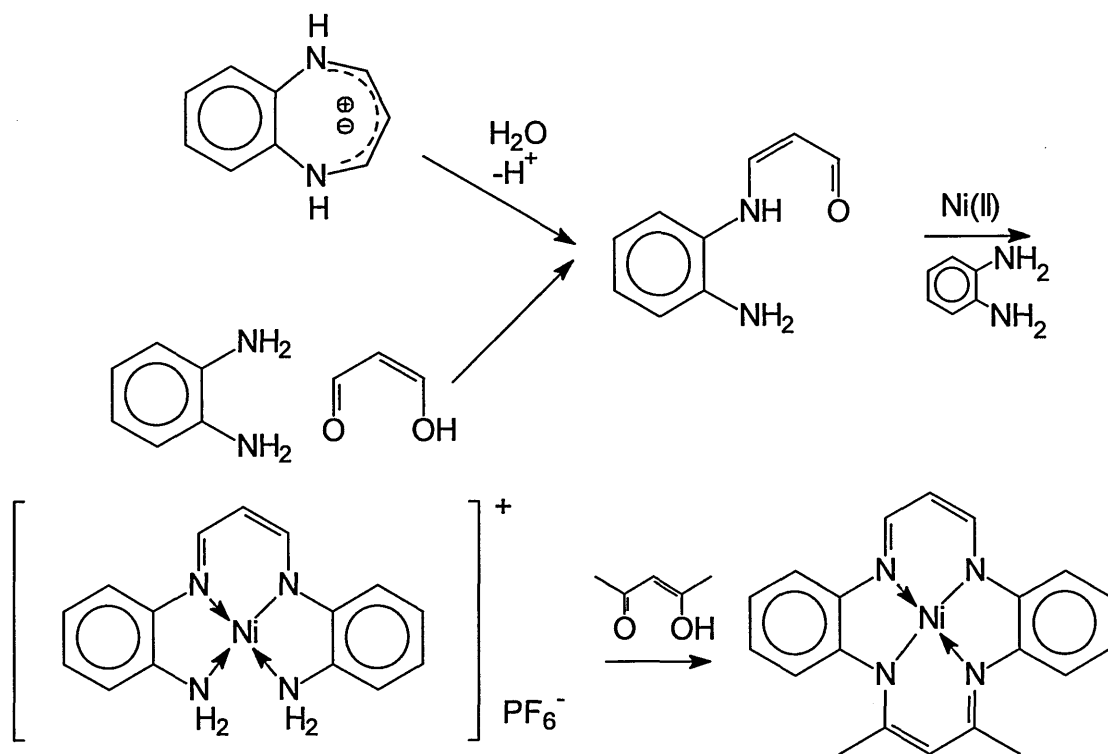


Fig. 4.20 Scheme for the preparation of unsymmetrical macrocycles.

However, it has been found that the construction of a more completely unsymmetrical DBTAA (i.e. two different aryl substituents also), is best achieved by a stepwise synthesis which involves the protection of the amino and/or carbonyl functionality of the precursors at various stages of the procedure, and the subsequent selective reaction of the acquired building blocks. The methodology of the procedure is discussed in chapter 5.

Chapter 5

Experimental Procedures

1. Introduction

The course of research into the synthesis and development of novel macrocyclic and polymeric materials, that have been structurally tailored to exhibit liquid crystalline and semi-conducting characteristics, has necessitated the use of a wide variety of synthetic procedures. In particular the preparation of substituted malondialdehydes²⁶⁹⁻²⁷¹, free ligand macrocycles and metal complexes of substituted dibenzotetraaza[14]annulenes, and the use of established synthetic procedures such as the Gabriel synthesis of amines²⁷² and the Wittig reaction^{273,274} has allowed the synthesis of an extensive array of new materials.

2. Apparatus and Techniques

Infra-red spectra were obtained on either a Pye- Unicam SP3-100 or Philips PU9700 spectrophotometer. ¹H and ³¹P NMR spectra were recorded on a Bruker 250 MHz, Bruker WP80SY and Jeol PMX 60 SI NMR spectrometers; CPMAS solid state ¹³C NMR was recorded on a Bruker UXR400 NMR spectrometer using a silicon reference probe. Samples were prepared in the solvent stated in each method. Microanalyses were performed by MEDAC Ltd of Brunel University. Melting points were determined on an electrothermal melting point apparatus. Mass spectra were recorded on a VG micromass instrument. Thermal characterisation was performed using a Mettler TC 10A thermogravimetric analyser and a Mettler TA 3000 differential scanning calorimeter. Thermal microscopy was investigated through crossed polarising filters.

Infra-red data are recorded as cm^{-1} of peak maxima. NMR data is expressed on the PPM scale with ¹H spectra recorded against tetramethylsilane as the internal reference standard.

abbreviations used for the form of the signal are as follows:

s	singlet
d	doublet
t	triplet
q	quartet
m	multiplet

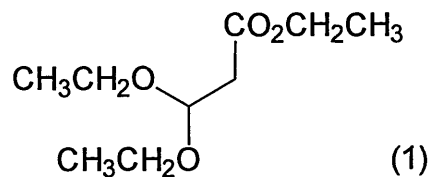
Flash chromatography and column chromatography were performed on Merck 7734 and Merck 7730 silica gel respectively. Thin layer chromatography was performed on Merck 5554 Autofolien Kieselgel 60F₂₅₄ plates.

When required anhydrous solvents were prepared according to established laboratory procedures. All reactions requiring inert atmospheres were performed under nitrogen.

3. Synthetic Procedures

Malondialdehydes and reaction intermediates

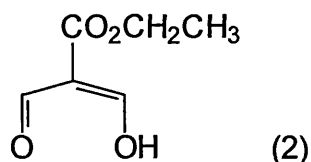
3.1 Ethyl 3,3-diethoxypropionate²⁷⁵ (1)



"Activated" zinc - Zinc dust (40g, 0.625mol.) was washed succesively with aqueous NaOH, water, aqueous acetic acid, water, ethanol, acetone and finally ether. The dust was then dried under vacuum at 100°C prior to use.

'Activated' zinc dust (34g, 0.53mol.) was suspended in dry benzene (40ml) and a crystal of iodine added. The mixture was brought to reflux and agitated by means of an overhead mechanical stirrer. A solution of ethyl bromoacetate (60.24g, 0.36mol.) and triethylorthoformate (53.5g, 0.36mol.) in dry benzene (340ml, 3.8mol.) was then added dropwise at a reasonably rapid drip rate with continued stirring, under reflux. After addition of the mixture was complete, heating and stirring was continued for one hour after which stirring was discontinued and the solution gently refluxed overnight. The zinc residues were decanted from the subsequently cooled solution which was then filtered, whilst the zinc residues were leached using hot 40/60 petroleum spirits (5 extractions) and filtered before addition to the benzene solution. The combined product mixture was evaporated to yield the crude product (50g, 0.26mol.) as a reddish brown oil. Vacuum distillation (50°C/0.1mmHg) afforded the main fraction as a colourless liquid (30g, 0.16mol., yield: 44%).

3.2 2-Carboethoxymalondialdehyde²⁷⁶ (2) - The Pannizzi Reaction



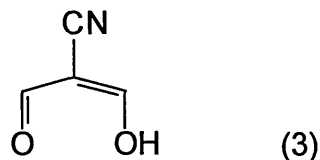
Under a super dry nitrogen atmosphere, a solution of ethyl-3,3-diethoxypropionate[†] (1) (11.8g, 0.06mol.) and ethyl formate[†] (9.25g, 0.12mol.) in anhydrous ether (5ml.) was added to small pieces of freshly cut sodium metal (2.88g, 0.13mol.) in anhydrous ether (50ml.). The flask was gently heated using a hair drier and once initiated the reaction proceeded satisfactorily at room temperature. The mixture was stirred for 4 hours and then gently refluxed for 1 hour. After cooling the residual sodium was destroyed by the CAREFUL addition of water (dropwise until all the sodium was destroyed). Water (100ml.) was added to the reaction mixture and the ether layer separated and set aside. The aqueous layer containing the product as its sodium salt was washed with ether (2 × 50ml.) and then carefully acidified with concentrated HCl_(aq.). Re-extraction with ether (3 × 50ml.) gave the crude product in the ether solution. The ether extract was dried (MgSO₄) and evaporated to yield a

ed/brown oil (6.55g,0.05mol.). The oil was purified by capillary air bleed vacuum distillation to give a pale yellow liquid (5g,0.034mol., yield: 57%).

- Esters must be dry. Pretreat with molecular sieves if necessary

Infra-red spectra	3200-3500cm ⁻¹	O-H stretch
	1720cm ⁻¹	C=O stretch
	1670cm ⁻¹	C=C stretch
Mass spectra	144	[M] ⁺
	116	
	99	[M-OCH ₂ CH ₃] ⁺
	88	
	73	[CO ₂ CH ₂ CH ₃] ⁺
¹ H NMR spectra	δ 1.5	t 3H
Solvent - CDCl ₃	δ 3.8	q 2H
	δ 7.5	s 2H
	δ 11.1	s 1H

3 2-Cyanomalondialdehyde²⁷⁵ (3)

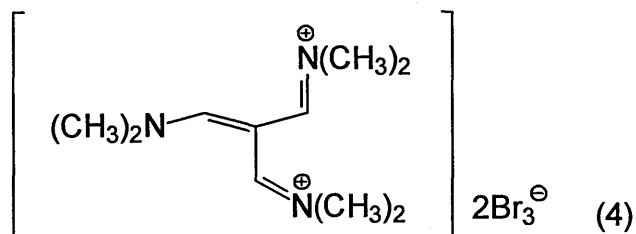


Under a super dry nitrogen atmosphere, a solution of 3,3-diethoxypropionitrile[†] (8.58g, 0.06mol.) and ethyl formate[†] (9.25g, 0.12mol.) in anhydrous ether (5ml.) was added to small pieces of freshly cut sodium metal (2.88g, 0.13mol.) in anhydrous ether (50ml.). The flask was gently heated using a hair drier and once initiated the reaction proceeded satisfactorily at room temperature. The mixture was stirred for 4 hours and then gently refluxed for 1 hour. After cooling the residual sodium was destroyed by the **CAREFUL** addition of water (dropwise until all the sodium was destroyed). Water (100ml.) was added to the reaction mixture and the ether layer separated and set aside. The aqueous layer containing the product as its sodium salt was washed with ether (2 × 50ml.) and then carefully acidified with concentrated HCl_(aq.). Re-extraction with ether (3 × 50ml.) gave the crude product in the ether solution. The ether extract was dried (MgSO₄) and evaporated to yield a red/brown oil (6.55g, 0.05mol.). The oil was purified by capillary air bleed vacuum distillation to give a red liquid (3.6g, 0.04mol., yield: 62%).

† - Esters and nitriles must be dry. Pretreat with molecular sieves if necessary

Infra-red spectra	3200-3550cm ⁻¹	O-H stretch
	2250cm ⁻¹	C≡N stretch
	1680cm ⁻¹	C=C stretch
Mass spectra	97	[M] ⁺
	96	[M-H] ⁺
	69/68/52	

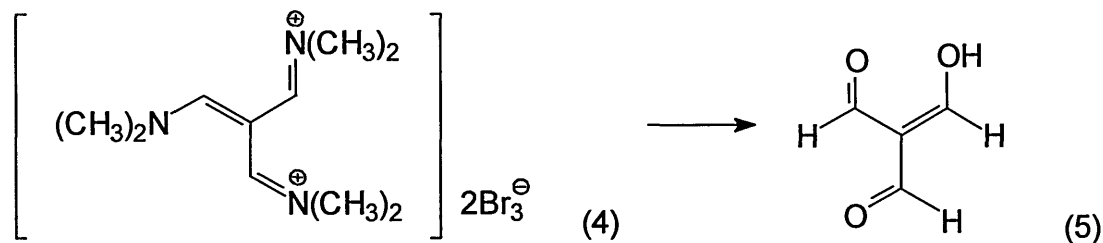
4 2-Dimethylamino-1,3-bis(dimethylimino)propane bis-perbromide²⁷⁷ (4)



To a stirred solution of bromoacetic acid (13.19g, 0.1mol.) in dimethylformamide (30.9ml., 0.4mol.) as added phosphoryl chloride (28ml., 0.3 mol.) over a period of 30 mins. at a temperature of 15°C. The mixture was allowed to stand for 30 min., and then heated with an oil bath to a temperature of 90 °C for 2 hours and 110°C for 7 hours. After cooling to room temperature the mixture was poured with stirring onto ice (300g). A solution of bromine (32g, 0.2 mol.) and sodium bromide (30.6g, 0.3 mol.) in water (70ml.) was added, and the stirring continued for 1 hour at approximately 10°C. The resulting orange precipitate was separated by suction, washed well with water, and dried in a vacuum desiccator over NaOH to give the required product (58.4g, 0.088mol. yield = 88%; m.p. 105-113°C. The crude salt was purified by dissolving it in acetonitrile, filtering and subsequently adding 1,2-dichloroethane. However it was often found that reactions proceeded satisfactorily using the crude product.

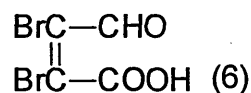
¹ H NMR spectra	δ 3.40	s 9H
Solvent - CDCl ₃	δ 3.55	s 9H
	δ 8.45	s 3H
Melting point	107-112°C	

.5 Triformylmethane²⁷⁷ (5)



To a stirred ice-cooled suspension of the perchlorate salt (4) (6.63g, 0.01 mol.) in H₂O (15ml.) was added solid sodium metabisulphite (2.85g, 0.015 mol.). After 15 mins. the pale yellow solution was made strongly alkaline by the gradual addition of excess solid sodium hydroxide (4g) at 20°C. After 45 mins. the mixture was cooled with an ice bath and dichloromethane (50ml.) along with conc. aq. HCl (10ml.) was added. A small portion of solid salts was removed by suction and the product extracted with dichloromethane (3 × 50ml.) and the combined extracts were dried with MgSO₄, filtered (charcoal) and evaporated to dryness to leave a residue (0.91g) that was purified by sublimation (0.82g, 0.008mol., yield = 82%; m.p. 104-106°C).

Infra-red spectra	3200-3600cm ⁻¹	O-H stretch
	2890cm ⁻¹	C-H stretch, aldehyde
	1700cm ⁻¹	C=O stretch
	1680cm ⁻¹	C=C stretch
Mass spectra	100	[M] ⁺
	72	
	71	[M-CHO] ⁺
	43	
¹ H NMR spectra	δ 9.1	broad s, 3H
Solvent - CDCl ₃	δ 12.6	s 1H

.6 Mucobromic acid^{278,279} (6)

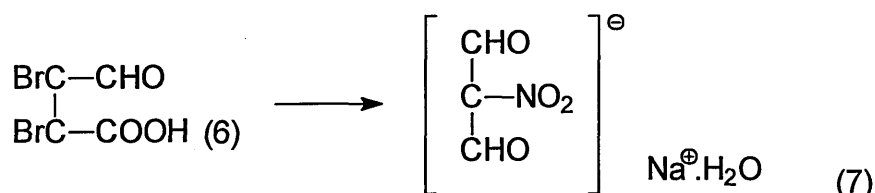
mixture of freshly distilled furfural (50g, 0.52 mol.) and water (500ml.) was placed in a 2-l. three necked round bottom flask fitted with a thermometer and dropping funnel. The flask was immersed in an ice/salt bath and bromine (450g, 2.81mol.) was added whilst the temperature was kept below 5°C.

After addition was complete, the thermometer was replaced by a reflux condenser and the reaction mixture stirred and boiled for 30 mins. The reflux condenser was subsequently replaced by a still head and condenser, and the excess bromine was removed by distillation until the distillate was almost colourless. The reaction mixture was evaporated to dryness under reduced pressure on a water bath using a liquid nitrogen cooled trap to condense the hydrobromic acid. The solid residue was cooled in an ice bath and triturated with 30-50ml of ice water. A few grams of sodium bisulphite were added to discharge a slight yellow discolouration. The cold mixture was filtered by suction to separate the crude mucobromic acid, which was washed with two small portions of cold water. The crude mucobromic acid (125g, 0.49mol., yield = 93%) was dissolved in boiling water (110ml.), decolourising carbon was added (2g), and the hot mixture stirred for 10 mins. after which it was filtered, and the filtrate cooled to 0-5°C. Colourless crystals of mucobromic acid were separated from the filtrate (100g, 0.39mol., yield = 75%; m.p. 124-125°C.)

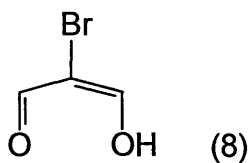
Infra-red spectra	2700-3250cm ⁻¹	O-H stretch, carboxylic acid
		C-H stretch, aldehyde
	2710cm ⁻¹	C=O stretch
	1725cm ⁻¹	C=C stretch
	1640cm ⁻¹	

mass spectra	258	$[M]^+$
	212	$[M-COOH]^+$
	177/179	$[M-Br]^+$
	133	
	131	$[M-COOH-Br]^+$

3.7 Sodium 2-nitromalondialdehyde monohydrate²⁸⁰ (7)



In a 100ml. three necked round bottom flask, equipped with a thermometer, dropping funnel and a gas vent was placed sodium nitrite (8.6g, 0.12 mol.) and water (10ml.). The contents of the flask were heated to dissolve the solid. Mucobromic acid (6) (8.6g, 0.03 mol.) in warm 95% ethanol (10ml.) was then placed in the dropping funnel and added dropwise with constant stirring over a period of 30 mins with the temperature kept at between 52-56°C. An exothermic reaction occurred with the solution in the flask becoming deep red and evolving gas. The mixture was stirred for an additional 10 mins at 52-56°C and then cooled to 0-5°C by the application of an ice bath under constant stirring. A fine yellow precipitate was collected on a previously chilled Büchner funnel. The slightly moist cake of crude product was transferred to a 50ml. flask and heated to boiling with 95% ethanol (15ml.) and water (4ml.). The hot solution was filtered to remove a fine yellow solid and the clear red filtrate cooled to 0-5°C. The recrystallised product was carefully collected on a Büchner funnel and dried in air at room temperature to yield the product as salmon pink needles (2.2g, 0.012mol.; yield = 41%).

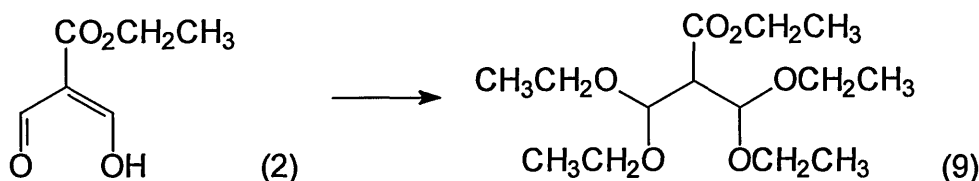
8 2-Bromomalondialdehyde^{281,282} (8)

o a vigorously stirred solution of malonaldehyde bis-(diethyl acetal) (100ml., 0.34mol.) in water (100ml.), was added concentrated hydrochloric acid (20ml.). To this bromine (17.5ml., 0.34ml.) was added dropwise with a resultant immediate decolourisation of the bromine (note- the rate of addition was kept sufficiently slow so that no increase in temperature was observed). The reaction mixture was taken down to a slush on a rotary evaporator (50°C), and filtered through a glass sinter. The pale yellow crystalline solid (29.35g, 0.19mol., 57%) was dried by suction and stored under nitrogen.

Infra-red spectra	3200-3550cm ⁻¹	O-H stretch, alcohols
	1750cm ⁻¹	C=O stretch
	1690cm ⁻¹	C=C stretch

Microanalysis	<u>Theory</u>	<u>Found</u>
Calculated for C ₃ H ₃ O ₂ Br	C 23.87%	C 24.05%
	H 2.00%	H 2.10%

9 2-Carboethoxymalondialdehyde bis(diethylacetal)²⁸³ (9)



Method 1 2-Carboethoxymalondialdehyde (2) (2.45g, 0.017mol.) and dry ethanol were placed in a 100ml. flame dried round bottom flask fitted with a CaCl₂ guard tube and a septum. Dry HCl gas (prepared by the addition of concentrated hydrochloric acid to concentrated sulphuric acid) was bubbled through the solution, with stirring, resulting in a colour change from yellow to deep red. The solution was used "as is" in further reactions.

Method 2 2-carboethoxymalondialdehyde (2) was distilled to yield a pale yellow product and stored over molecular sieve. Ethanolic HCl was prepared by bubbling dry HCl gas through dry ethanol for 90 minutes, and was stored over molecular sieve.

Ethanolic HCl (20ml.) was placed in a flame dried 100ml. round bottom flask fitted with a CaCl₂ guard tube. To this was added distilled 2-carboethoxymalondialdehyde (2) (0.7g, 4.9mmol.) resulting in the formation of an instantaneous red colouration; the solution was stirred overnight. The excess HCl was neutralised by the addition of a suspension of solid sodium carbonate in a saturated sodium bicarbonate solution resulting in a colour change from red to yellow. The solution was filtered to remove excess sodium carbonate and the ethanol was removed under reduced pressure on a rotary evaporator at 50°C. The evaporation resulted in the isolation of a yellow solid which was assumed to be a mixture of sodium carbonate, sodium bicarbonate and the required acetal. The solid was dissolved in a mixture of water (50ml.) and dichloromethane (50ml.) and the solution placed in separating funnel. The aqueous layer was removed and the dichloromethane was washed with saturated brine (2 × 50ml.) before being dried with MgSO₄ and evaporated under reduced pressure to yield an amber liquid (0.12g). Examination of the product by TLC using dichloromethane as the

evolving solvent shows reaction to have occurred but that the product contains many components.

certain spots gave a positive test for aldehydes when sprayed with dinitrophenylhydrazine.

Mass spectra	The mass spectra was very complex. High molecular weight fragments were observed
Base peak 103	$[(\text{CH}_3\text{CH}_2)_2\text{OCH}]^+$

Method 3 2-carboethoxymalondialdehyde (2) was distilled to yield a pale yellow product and stored over molecular sieve. Ethanolic HCl was prepared by bubbling dry HCl gas through dry ethanol for 90 minutes and was stored over molecular sieve.

Ethanolic HCl (20ml.) was placed in a flame dried 100ml. round bottom flask fitted with a CaCl_2 guard tube. To this was added distilled 2-carboethoxymalondialdehyde (2) (0.6g, 4.2mmol.) resulting in the formation of an instantaneous red colouration; the solution was stirred for 48 hours. The ethanol and HCl gas was then removed by evaporation under reduced pressure at 50°C to yield a beige viscous semi-solid. This was triturated under dry ether to give a beige powder (0.8g) which was hygroscopic and soon became wet in appearance.

Mass spectra	313	
	38	$[\text{HCl}]^+$
	36	$[\text{HCl}]^+$ - Isotope splitting pattern for chlorine.

Method 4 2-carboethoxymalondialdehyde (2) was distilled to yield a pale yellow product and stored over molecular sieve. Ethanolic HCl was prepared by bubbling dry HCl gas through dry ethanol for 90 minutes and was stored over molecular sieve.

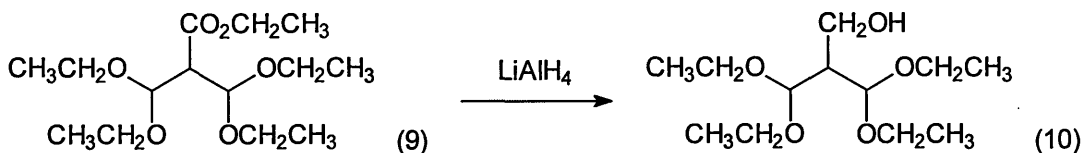
ethanolic HCl (20ml.) was placed in a flame dried 100ml. round bottom flask fitted with a CaCl₂ guard tube. To this was added distilled 2-carboethoxymalondialdehyde (2) (3.15g, 0.021mol.) resulting in the formation of an instantaneous red colouration; the solution was refluxed for 2 hours under nitrogen. The excess HCl was neutralised by the addition of a suspension of solid sodium carbonate in a saturated sodium bicarbonate solution resulting in a colour change from red to yellow. The solution was filtered to remove excess sodium carbonate and the ethanol was removed under reduced pressure on a rotary evaporator at 50°C. The evaporation resulted in the isolation of a yellow solid which was assumed to be a mixture of sodium carbonate, sodium bicarbonate and the required acetal. The solid was dissolved in a mixture of water (50ml.) and dichloromethane (50ml.) and the solution placed in separating funnel. The aqueous layer was removed and the dichloromethane was washed with saturated brine (2 × 50ml.) before being dried with MgSO₄ and evaporated under reduced pressure to yield a dark liquid (1.0g, 3.4mmol., Yield = 16%). Examination of the product by LC using dichloromethane as the developing solvent shows two spots at R_f values of 0.36 and 0.44 (with an additional faint tailing peak at an R_f of 0.21 which was found to be 2-carboethoxymalondialdehyde). Both spots show a negative response to dinitrophenylhydrazine indicating the absence of aldehydes.

Mass spectra	279	
	103	[(CH ₃ CH ₂) ₂ OCH] ⁺
	75/47	
Infra-red spectra	3200-3600cm ⁻¹	O-H str.
	2970cm ⁻¹ and 2920cm ⁻¹	C-H str. - aliphatic
	1730cm ⁻¹	C=O str. - esters
	1440cm ⁻¹ and 1370cm ⁻¹	C-H bend - aliphatic
	1110cm ⁻¹ and 1050cm ⁻¹	C-O str. - esters

ethod 5 - Acetalisation via the Arnold procedure²⁷⁷ 2-Carboethoxy malondialdehyde† (2) (0.72g, mmol.) was stirred in a mixture of triethylorthoformate (5ml., 30mmol.) and ethanol (1ml.) for 5 minutes. To this was added 70% HClO₄ (approx. 10mg) and the mixture was allowed to stand overnight. The acid was neutralised with a 1M solution of NaOH in methanol. Volatile material was removed under reduced pressure on a rotary evaporator and the product purified by vacuum distillation to give a colourless liquid (1.04g, 3.6mmol., 72%).

Mass spectra	241/201/169	
	103	[(CH ₃ CH ₂) ₂ OCH] ⁺
	75/41	
¹ H NMR spectroscopy	δ 1.2	t, 12H - (CH ₃ CH ₂ O) ₂ -CH
	δ 1.3	t, 3H - COOCH ₂ CH ₃
	δ 1.55	s - (CH ₃ CH ₂ O) ₂ -CH*
	δ 3.45	s - (CH ₃ CH ₂ O) ₂ -CH*
	δ 3.7	q, 8H - (CH ₃ CH ₂ O) ₂ -CH
	δ 4.2	q, 2H - COOCH ₂ CH ₃
	δ 8.05	s, 1H - OH, Hydrogen bonded ∴ lower field.
		* Appropriate chemical shift but incorrect multiplicity.

.10 2-Hydroxymethylenemalondialdehyde bis(diethyl acetal) (10)



Method 1 2-Carboethoxymalondialdehyde bis(diethylacetal) (9), (3.9 method 1), was placed in a flame dried 100ml. round bottom flask fitted with a CaCl₂ guard tube. A suspension of LiAlH₄ in dry ether (20ml.) was prepared and added dropwise to the flask with stirring and cooling (ice bath) which resulted in the formation of a greyish blue solution. Excess LiAlH₄ was destroyed by the addition of ethyl acetate (20ml.) and liberation of the free alcohol achieved by the addition of concentrated NaOH (5ml.); this resulted in the formation of a deep red/black colour. The resulting solution was extracted with ether (3 × 50ml.) and dried with MgSO₄ before the ether was removed under reduced pressure by rotary evaporation to give a deep red/black liquid (1.1g, 4.4mmol., Yield = 26%).

Infra-red spectra	3450cm ⁻¹	O-H str. - alcohols
	2970cm ⁻¹	C-H str. - aliphatic
	1720cm ⁻¹	C=O str. - carbonyls
¹ H NMR spectroscopy	δ 1.2	t, 12H - OCH ₂ CH ₃
	δ 1.3	quintet, 1H - CH-CH ₂ OH
	δ 3.25 - 4.0	q, 8H - OCH ₂ CH ₃
	δ 3.6	d, 2H - CH ₂ OH
	δ 4.2	d, 2H - (CH ₃ CH ₂ O) ₂ -CH
	δ 0 - 4.5	CH ₂ OH absent, may be hidden under other peaks

Mass spectra	242/225/211/197/183/169	
	103	$[(\text{CH}_3\text{CH}_2)_2\text{OCH}]^+$

Method 2 2-Carboethoxymalondialdehyde bis(diethyl acetal) (9) (1g, 3.4mmol.) [3.9 method 4] was dissolved in dry tetrahydrofuran (10ml.) and the mixture was cooled in ice in a flame dried 50ml. round bottom flask fitted with a CaCl_2 guard tube. Reduction of the ester was attempted by the CAREFUL addition of LiAlH_4 (0.3g, 8mmol) in portions over a period of 30 minutes. The reaction mixture was stirred for 30 minutes before the excess LiAlH_4 was destroyed by the dropwise addition of 2M NaOH until effervescence ceased. The solution was then made strongly alkaline by further addition of 2M NaOH and extracted with ether ($2 \times 50\text{ml.}$). The ether layer was dried with MgSO_4 and evaporated to yield a yellow liquid (0.15g, 0.6mmol., Yield = 18%).

Mass spectra	277/195	
	103	$[(\text{CH}_3\text{CH}_2)_2\text{OCH}]^+$
	75/47	

Infra-red spectra	$3600\text{-}3200\text{cm}^{-1}$ (weak)	O-H str. - alcohol
	$2970\text{-}2925\text{cm}^{-1}$	C-H str. - aliphatic
	1440cm^{-1} and 1330cm^{-1}	C-H bend - aliphatic
	$1240\text{-}950\text{cm}^{-1}$	C-O str. - ether or esters

Method 3 2-Carboethoxymalondialdehyde bis(diethyl acetal) (9) (0.5g, 1.7mmol.) [3.9 method 5] was dissolved in dry ether (20ml.) and placed in a flame dried 50ml. round bottom flask fitted with a CaCl_2 guard tube. The reduction of the ester was attempted by the CAREFUL addition of LiAlH_4 in portions and the mixture was stirred overnight. Excess LiAlH_4 was destroyed by the dropwise addition of water until effervescence ceased. The reduced acetal (10) was isolated by the dropwise addition of 2M

aOH (20ml.), followed by isolation of the ether layer. The ether layer was dried with MgSO_4 and vaporated under reduced pressure to give a colourless liquid (0.38g).

Infra-red spectra	3600-3100 cm^{-1}	O-H str. - alcohol
	2970 cm^{-1}	C-H str. - aliphatic
	1375 cm^{-1} , 1445 cm^{-1} and	
	1340 cm^{-1}	C-H bend - aliphatic
^1H NMR spectroscopy	δ 1.2	t - CH_3
	δ 3.35	s - OH
	δ 3.5	q - CH_2
		The above data indicated that the liquid is a mixture of ethanol and ether

Aqueous layer work up Half of the aqueous layer was extracted with dichloromethane ($5 \times 30\text{ml.}$) to attempt to afford the reduced acetal. No product was isolated.

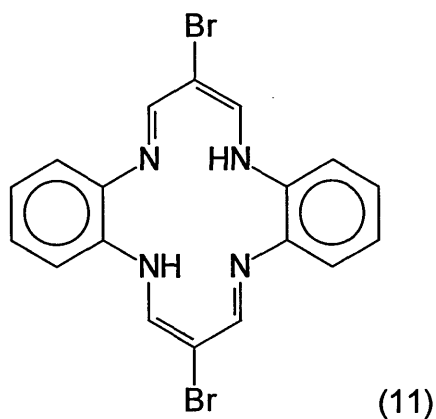
The remaining half of the aqueous layer was acidified with $2\text{M H}_2\text{SO}_4$ and extracted with ether ($3 \times 30\text{ml.}$). The ether layer was dried with MgSO_4 and evaporated to yield a colourless liquid with some solid precipitate (0.46g).

Mass spectra	98/81/80/64/48	Expected molecular ion at m/z of 102.
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H NMR spectroscopy	δ 1.25	t, 2H
	δ 1.65	s, 15H
	δ 3.75	q, 1.5H
	δ 5.0	s, 106H
	δ 7.25	s, 3H

ymmetrical macrocyclic ligands

.11 6,13-dibromodibenzo[b,i][1,4,8,11]tetraazacyclotetradecine²⁸⁴ (11)



2-Bromomalondialdehyde (8) (1.08g, 0.01 mol.) in cold ethanol (20ml.) was added to a stirred solution of ortho-phenylenediamine (1.51g, 0.01mol.) in cold ethanol (30ml.). The mixture was stirred in the dark overnight, after which a precipitate appeared that was filtered and washed with cold ethanol to yield a brown solid (0.42g, 1.0mmol, Yield = 19%). A sacrificial recrystallisation with chloroform (100ml.) and the required amount of methanol produced the pure crystalline macrocycle.

Mass spectra

The mass spectra is complex and difficult to analyse. The expected high molecular weights are absent although the splitting pattern of bromine is observed at lower molecular weights.

Microanalysis

Theory

Found

Calculated for $C_{18}H_{14}N_4Br_2$

C 48.45%

C 48.49%

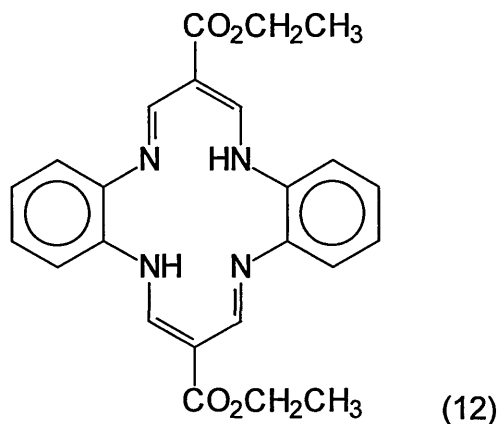
H 3.16%

H 2.81%

N 12.55%

N 12.90%

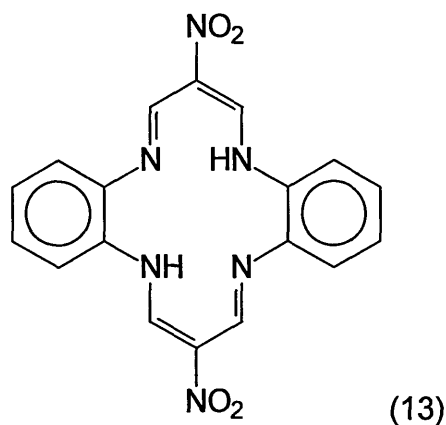
3.12 6,13-dicarboethoxy-dihydrodibenzo[b,i][1,4,8,11]tetraazacyclotetradecine¹⁰⁴ (12).



2-Carboethoxymalondialdehyde (2) (4g, 0.027mol.) was dissolved in dry methanol (45ml.). To this as added a solution of ortho-phenylenediamine (3.0g, 0.027mol.), along with a catalytic quantity of para-toluenesulphonic acid, dissolved in dry methanol (60ml.). The reaction mixture was stirred in the dark for 60 hours, and then filtered to yield a bright orange solid. A sacrificial recrystallisation with chloroform (100ml.) and the required amount of methanol produced the pure crystalline macrocycle (0.65g, 1.5mmol., Yield = 11%). Conventional recrystallisation led to a contaminated product.

Mass spectra	432	$[M]^+$
	359	$[M-CO_2CH_2CH_3]^+$
	313/241/174/119	
Microanalysis	<u>Theory</u>	<u>Found</u>
Calculated for $C_{18}H_{14}N_4O_4$	C 66.65%	C 64.78%
	H 5.59%	H 6.99%
	N 12.96%	N 11.88%

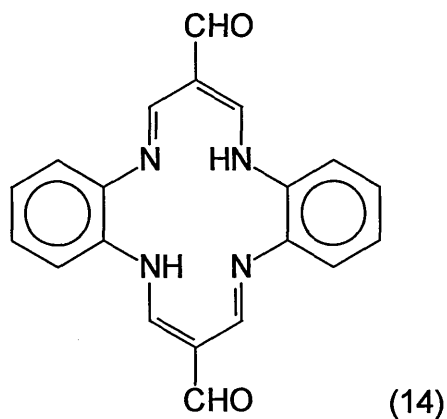
3.13 6,13-dinitro-dihydrodibenzo[b,i][1,4,8,11]tetraazacyclotetradecine¹⁰⁴ (13)



The sodium salt of 2-nitromalondialdehyde (7) (0.9g, 6.5mmol.) was dissolved in dry methanol (16ml.) containing glacial acetic acid (1ml.). To this was added a solution of ortho-phenylenediamine (0.7g, 6.5mmol.) in dry methanol (16ml.). The reaction mixture was stirred in the dark for 60 hours. The precipitated macrocycle was filtered and purification achieved by a sacrificial recrystallisation with chloroform (50ml.) and methanol, to yield a sparingly soluble red powder (0.25g, 0.7mmol., Yield = 11%).

Mass spectra	378	[M] ⁺
	285/168/119	
Microanalysis	<u>Theory</u>	<u>Found</u>
Calculated for C ₁₈ H ₁₄ N ₆ O ₄	C 61.71%	C 61.53%
	H 4.02%	H 4.29%
	N 15.99%	N 14.84%

14 6,13-diformyl-dihydrodibenzo[b,i][1,4,8,11]tetraazacyclotetradecine (14)



Method 1 Ortho-phenylenediamine (0.27g, 2.5mmol.) was placed in a 50ml. round bottom flask along with dry tetrahydrofuran (10ml.) and a catalytic quantity of para-toluenesulphonic acid. The mixture was brought to reflux under nitrogen, and triformylmethane (5) (0.25g, 2.5mmol.) in tetrahydrofuran (10ml.) was added. The reaction mixture was refluxed under nitrogen for a further 1½ hours. The solution was cooled in ice and filtered to yield a red/brown solid (0.22g, 0.6mmol., Yield = 24%, m.p. 272-274°C). A sacrificial recrystallisation with chloroform (100ml.) and the required amount of methanol failed to produce the pure crystalline macrocycle.

Mass spectra	344	[M] ⁺
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225/197/158/118

Microanalysis

The data did not correspond to the expected formula

$C_{20}H_{16}N_4O_2$ presumably due to the presence of impurities.

Method 2 Triformylmethane (5) (0.9g, 9mmol.) was dissolved in dry ethanol (40ml.), with slight warming. This was added to a slight excess of ortho-phenylenediamine (1.08g, 0.01mol.) in dry ethanol (40ml). The reaction mixture was stirred in the dark, overnight, at room temperature. Isolation of the macrocycle (1.4g, 4mmol., Yield = 44%) by filtration, was followed by a sacrificial recrystallisation using chloroform (50ml.) and ethanol.

Mass spectra	344	[M] ⁺
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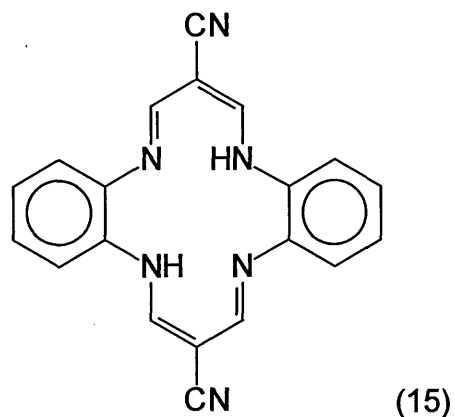
225/197/158/118

Microanalysis

The data did not correspond to the expected formula

$C_{20}H_{16}N_4O_2$ presumably due to the presence of impurities.

.15 6,13-dicyano-dihydrodibenzo[b,i][1,4,8,11]tetraazacyclotetradecine (15)



Ortho-phenylenediamine (0.26g, 2.5mmol.) was placed in a 50ml. round bottom flask along with dry tetrahydrofuran (10ml.) and a catalytic quantity of para-toluenesulphonic acid. This was brought to reflux under nitrogen, and 2-cyanomalondialdehyde (3) (0.25g, 2.5mmol.) in tetrahydrofuran (10ml.) was added. The reaction mixture was refluxed under nitrogen for a further 1½ hours. The solution was cooled in ice and filtered to yield a red/brown solid (0.24g, 0.6mmol., Yield = 24%). A sacrificial recrystallisation with chloroform (100ml.) and the required amount of methanol failed to produce the pure crystalline macrocycle.

Mass spectra

338

$[M]^+$

310

$[M-CN]^+$

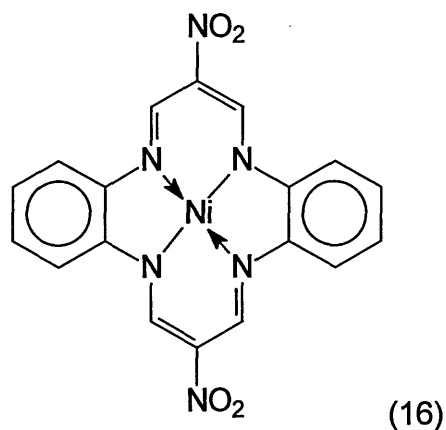
Microanalysis

The data did not correspond to the expected formula

$C_{20}H_{14}N_6$ presumably due to the presence of impurities.

Asymmetrical macrocyclic complexes of nickel and reaction intermediates

6,13-dinitro-dihydrodibenzo[b,i][1,4,8,11]tetraazacyclotetradecine Nickel (II)²⁸⁵ (16)



The sodium salt of 2-nitromalondialdehyde (7) (0.9g, 6.5mmol.) was dissolved in dry methanol (16ml.) containing glacial acetic acid (1ml.). To this was added a solution of ortho-phenylenediamine (0.7g, 6.5mmol.) in dry methanol (16ml.), and a solution of nickel(II) acetate tetrahydrate (0.81g, 3.3mmol.) in dry methanol (10ml.). The reaction mixture was stirred in the dark for 60 hours. The precipitated macrocycle was filtered and purification achieved by a sacrificial recrystallisation with chloroform (50ml.) and methanol, to yield a sparingly soluble red powder (1.33g, 3.1mmol., Yield = 68%).

Mass spectra

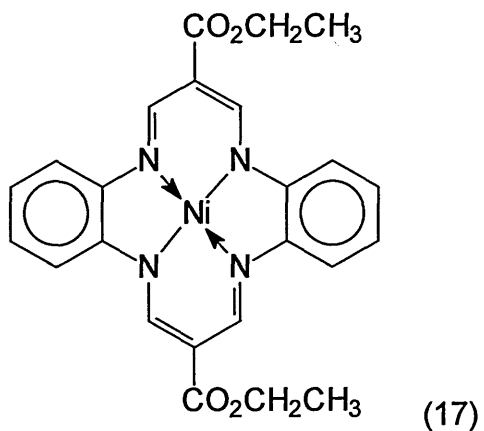
The spectrum was complex with no discernible molecular ion

Microanalysis

The data did not correspond to the expected formula

$C_{18}H_{12}N_6O_4Ni$ presumably due to the presence of impurities.

.17 6,13-dicarboethoxy-dihydrodibenzo[b,i][1,4,8,11]tetraazacyclotetra decine Nickel (II) (17)



Nickel(II) acetate tetrahydrate (0.06g, 0.24mmol.) in dimethylformamide (10ml.) was added to a stirred solution of 6,13-dicarboethoxy-dihydrodibenzo[b,i][1,4,8,11] tetraazacyclotetradecine (12) (0.1g, 0.23mmol.) in dimethylformamide (50ml.). The reaction mixture was stirred in the dark overnight to yield an orange solid (0.06g, 0.12mmol., Yield = 50%), this was later purified by soxhlet extraction with dichloromethane.

Mass spectra

488

$[M]^+$

432

$[M-Ni]^+$

313/241/174/119

Microanalysis

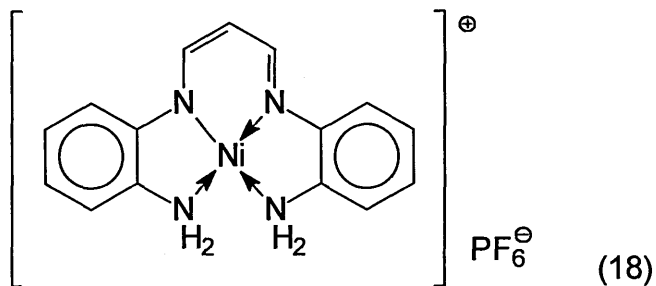
The data did not correspond to the expected formula

$C_{24}H_{22}N_4O_4Ni$ presumably due to the presence of

impurities.

.18 [N,N''-(1,3-propanediylidene)bis(1,2-benzenediaminato)-[N,N',N'', N''']nickel(II)

hexafluorophosphate²⁸⁶ (18)

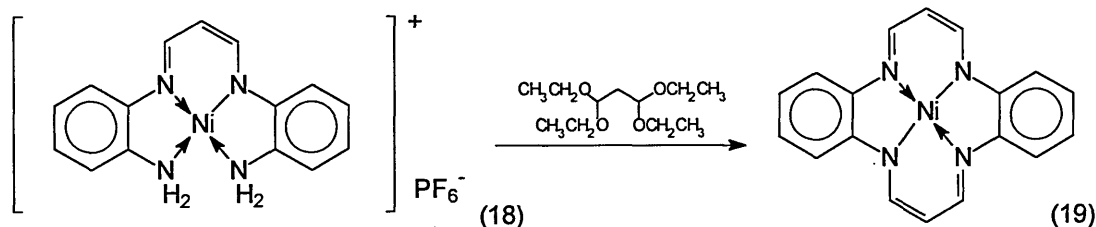


An aqueous suspension (150ml.) of ortho-phenylenediamine(4.3g, 0.04 mol.), 1,1,3,3-tetramethoxy propane (3.4ml., 0.02mol.), nickel(II) chloride hexahydrate (4.8g, 0.02mol.), and ammonium hexafluoro phosphate (10g, 0.06mol.) was heated in a 250ml. round bottomed flask. The blue/grey suspension became a dark green solution after 15 mins. of heating, before turning reddish/brown and producing a purple/brown suspension and foam after refluxing for a further 20 mins. Cooling and then filtering the thick suspension gave a red/brown solid and lemon yellow filtrate. The solid was washed with cold water (3 × 30ml.), air dried for 18 hours, and redissolved in acetone (40ml.). Dropwise addition of the filtered solution into excess ether (450ml.) precipitated a granular red/brown solid which was dried under vacuum (6g, 0.013mol., Yield = 65%).

1H NMR spectra	δ 3.3	Broad s, 4H, -NH ₂
Solvent: Acetone-d ₆	δ 5.62	t and broad s, 3H, C-CH-C
	δ 6.9-7.9	m, 8H, Ar-H

Microanalysis	Theory	Found
Calculated for	C 39.60%	C 40.05%
C ₁₅ H ₁₅ N ₄ NiPF ₆	H 3.32%	H 3.43%
	N 12.31%	N 12.60%

.19 Dihydrodibenzo [b,i][1,4,8,11]tetraazacyclotetradecine Nickel (II)²⁸⁷ (19)



[N,N''-(1,3-propanediylidene) bis(1,2-benzene diaminato)-N,N',N'',N''']nickel(II) hexafluorophosphate (18) (1g, 2.2mmol.) was dissolved in a 90% aqueous solution of dimethylformamide (40ml.). To this was added 1,1,3,3-tetramethoxypropane (0.36g, 2.2 mmol.) dropwise with stirring, and the whole was refluxed for 10 hours under nitrogen . The solution was cooled and filtered to yield a dark purple solid which was washed with water (3 × 30ml.) and the solid product air dried (0.4g, 2.16 mmol., Yield = 98%).

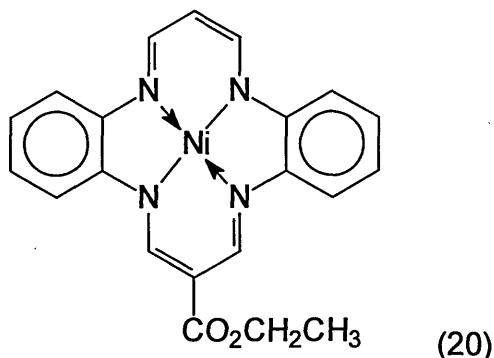
Mass spectra	345	[M] ⁺
	344	[M-H] ⁺
	172/58	

¹H NMR spectra The sample was found to be insoluble in available NMR solvents.

Microanalysis	Theory	Found
Calculated for C ₁₈ H ₁₄ N ₄ Ni	C 62.66%	C 62.44%
	H 4.09%	H 4.12%
	N 16.24%	N 16.18%

-D Unsymmetrical macrocyclic complexes of nickel (II)

.20 6-Carboethoxy-dihydrodibenzo[b,i][1,4,8,11]tetraazacyclotetra decine Nickel (II) (20)



[N,N''-(1,3-propanediylidene) bis(1,2-benzene diaminato)-N,N',N'',N''']nickel(II) hexafluorophosphate (18) (1g, 2.2mmol.) was dissolved in a 90% aqueous solution of dimethylformamide (40ml.). To this carboethoxymalondialdehyde (2) (0.32g, 2.2mmol.) dissolved in 90% aqueous dimethylformamide (10ml.) was added dropwise with stirring and the whole was refluxed under nitrogen for 10 hours. The resulting solution was cooled and poured into water (400ml.). The precipitated solid was filtered under suction, washed with water (3 × 30ml.) and subsequently air dried to yield the macrocycle as a brown solid (0.6g, 1.4mmol., Yield = 64%).

Mass spectra

417

[M]⁺

402

[M-CH₃]⁺

388

[M-CH₂CH₃]⁺

344

[M-COOCH₂CH₃]⁺

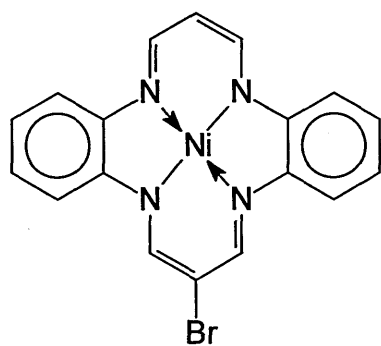
Microanalysis

The data did not correspond to the expected formula

C₂₁H₁₈N₄O₂Ni presumeably due to the presence of

impurities.

3.21 6-Bromo-dihydrodibenzo[b,i][1,4,8,11]tetraazacyclotetradecine Nickel (II) (21)



(21)

[N,N''-(1,3-propanediylidene) bis(1,2-benzene diaminato)-N,N',N'',N''']nickel(II) hexafluorophosphate (18) (1g, 2.2mmol.) was dissolved in a 90% aqueous solution of dimethylformamide (40ml.). To this bromomalondialdehyde (8) (0.33g, 2.2mmol.) dissolved in 90% aqueous dimethylformamide (10ml.) was added dropwise with stirring and the whole was refluxed under nitrogen for 10 hours. The resulting solution was cooled and poured into water (400ml.). The precipitated solid was filtered under suction, washed with water (3 × 30ml.) and subsequently air dried to yield the macrocycle as a brown solid (0.53g, 1.3mmol., Yield = 59%).

Mass spectra

344

[M-Br]⁺

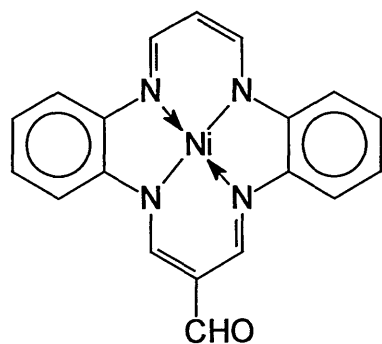
Microanalysis

The data did not correspond to the expected formula

C₁₈H₁₃N₄BrNi presumably due to the presence of

impurities.

3.22 6-Formyl-dihydrodibenzo[b,i][1,4,8,11]tetraazacyclotetradecine Nickel (II) (22)



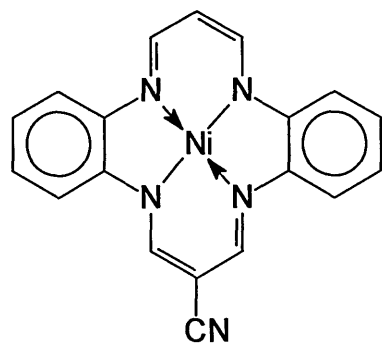
(22)

[N,N''-(1,3-propanediylidene) bis(1,2-benzenediaminato)-N,N',N'',N''']nickel(II) hexafluorophosphate (18) (1g, 2.2mmol.) was dissolved in a 90% aqueous solution of dimethylformamide (40ml.). To this trimethylmethane (5) (0.22g, 2.2mmol.) dissolved in 90% aqueous dimethylformamide (10ml.) was added dropwise with stirring and the whole was refluxed under nitrogen for 10 hours. The resulting solution was cooled and poured into water (400ml.). The precipitated solid was filtered under suction, washed with water (3 × 30ml.) and subsequently air dried to yield the macrocycle as a brown solid (0.5g, 1.3mmol., Yield = 76%).

Mass spectra	373	[M] ⁺
	372	[M-H] ⁺
	344	[M-CHO] ⁺

Microanalysis The data did not correspond to the expected formula C₁₉H₁₄N₄ONi presumably due to the presence of impurities.

3.23 6-Cyano-dihydrodibenzo[b,i][1,4,8,11]tetraazacyclotetradecine Nickel (II) (23)



(23)

[N,N''-(1,3-propanediylidene) bis(1,2-benzene diaminato)-N,N',N'',N''']nickel(II) hexa fluorophosphate (18) (1g, 2.2mmol.) was dissolved in a 90% aqueous solution of dimethylformamide (40ml.). To this cyanomalondialdehyde (3) (0.21g, 2.2mmol.) dissolved in 90% aqueous dimethylformamide (10ml.) was added dropwise with stirring and the whole was refluxed under nitrogen for 10 hours. The resulting solution was cooled and poured into water (400ml.). The precipitated solid was filtered under suction, washed with water (3 × 30ml.) and subsequently air dried to yield the macrocycle as a brown solid (0.32g, 0.9mmol., Yield = 41%).

Mass spectra

370

[M]⁺

344

[M-CN]⁺

Microanalysis

The data did not correspond to the expected formula

Analytically calculated for

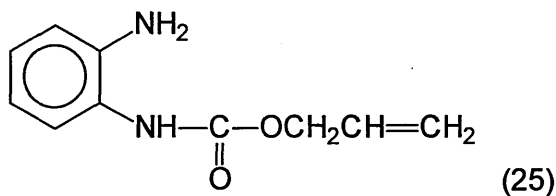
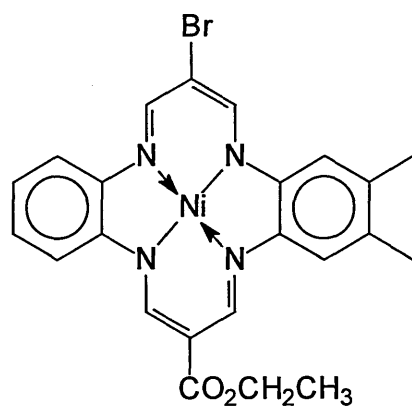
C₁₉H₁₃N₅Ni presumeably due to the presence of impurities.

C₂₁H₁₈N₄O₂Ni

2-D Unsymmetrical macrocyclic complexes of nickel (II) and reaction intermediates

3.24 6-Carboethoxy-13-bromo-dihydrobenzo-4,5-dimethylbenzo[b,i][1,4,8,11]

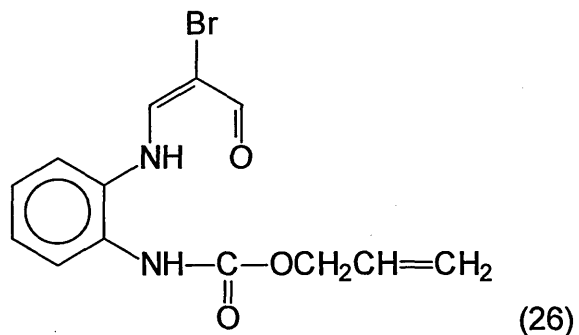
tetraazacyclotetradecine nickel (II) (24)



Stage 1 Ortho-phenylenediamine (2.8g, 0.026mol.) dissolved in dichloromethane (25ml.) was stirred vigorously with a solution of sodium hydroxide (1M, 1.12g in 28ml. water). To this a solution of allyl chloroformate (3.2g, 0.027mol.) in dichloromethane (10ml.) was added dropwise. After complete addition the mixture was stirred for a further ½ hour, then extracted with dichloromethane, dried and the solvent removed under vacuum to leave an orange/brown oil. This was triturated under petrol to give a beige powder (3.98g). The crude product contained a mixture of mono- and bis-protected derivatives. The required mono-protected product (25) was isolated after chromatography on silica gel with an eluant of ethyl acetate/petrol/chloroform (20:30:50). The solvent was removed by rotary evaporation to yield the product as an off-white powder (2.3g, 0.012mol., Yield = 46%)

Melting point	81-82°C	
Infra-red spectra	3460cm ⁻¹	N-H stretch
	3380cm ⁻¹	N-H stretch
	1720cm ⁻¹	C=O stretch
	1640cm ⁻¹	C=C stretch
¹ H NMR spectra	δ 3.7	s, 2H, exchange by D ₂ O,
Solvent - CDCl ₃		NH ₂
	δ 4.6	d, 2H, CH=CH ₂
	δ 5.2-6.2	m, 3H, CH=CH ₂
	δ 6.5	broad s, 1H, NH - Urethane
	δ 6.7-7.4	m, 4H, Aryl-H
Mass Spectra	192	[M] ⁺
	134	
	107	[M-C ₄ H ₅ O ₂] ⁺
	80/41	
Microanalysis	<u>Theory</u>	<u>Found</u>
Calculated for C ₁₀ H ₁₂ N ₂ O ₂	C 62.49%	C 62.52%
	H 6.29%	H 6.24%
	N 14.57%	N 14.63%

Stage 2 Bromomalondialdehyde (8) (0.24g, 1.59mmol.) was dissolved in tetrahydrofuran (10ml.) and heated to boiling, under nitrogen, with a catalytic quantity of para-toluenesulphonic acid. Mono-protected diamine (25) (0.3g, 1.56mmol.) in tetrahydrofuran was added to the refluxing mixture, giving an immediate red solution, which was refluxed overnight, under nitrogen. The cooled mixture was poured, with stirring into petroleum spirits (40/60) (100ml.) and the resultant pale yellow solid (26) was filtered and washed with ether, then air dried (0.45g, 1.41mmol., Yield = 89%).



¹H NMR spectra

δ 4.7

d, 2H

Solvent - CDCl₃

δ 5.2-6.2

m, 3H

δ 6.85

broad s, 1H

δ 7.2

m, 4H

δ 7.7

d, 1H

δ 8.6

broad d, 1H

δ 9.1

s, 1H

Mass Spectra

324

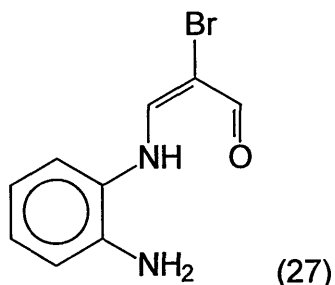
[M]⁺

239

[M-C₄H₅O₂]⁺

203/159/131/119/41

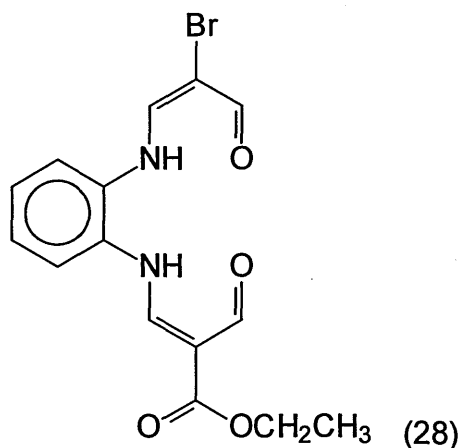
Stage 3 A mixture of the mono-protected mono-anil (26) (0.2g, 0.62mmol.), triphenylphosphine (0.066g) and tetrakis (triphenylphosphine)palladium (0) (0.015g) was stirred in dry ether (2ml.) before the addition of 2-ethylhexanoic acid (0.22g, 1.52mmol.) in ether (1ml.). The resultant yellow suspension was then stirred under nitrogen, in the dark for 1 hour. The product could then be identified by TLC when sprayed with a solution of Ehrlichs reagent (para-dimethylaminobenzaldehyde). The crude mixture was purified by column chromatography using silica gel and ethyl acetate/petrol/chloroform (20/30/50) as the eluant. On evaporation of the solvent a pale orange powder (27) was obtained (52mg., 0.22mmol., Yield = 35%).



Infra-red spectra	3390cm ⁻¹	N-H stretch
	3320cm ⁻¹	N-H stretch
Mass Spectra	240	[M] ⁺
	161	[M-Br] ⁺
	132/119/65	

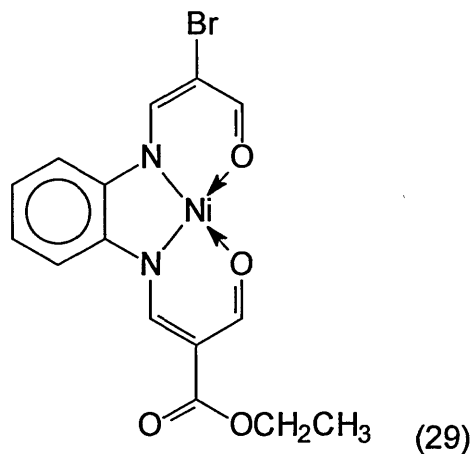
Stage 4 The mono-anil (27) (0.26g, 1.08mmol.) was dissolved in warm tetrahydrofuran (7 ml.) and added to a refluxing solution of 2-carboethoxymalondialdehyde (2) (0.78g, 5.4mmol.) in tetrahydrofuran (10ml.) under nitrogen. Reflux was continued for 3 hours after which the solution was cooled and then added dropwise, with stirring into petrol (100ml.). The resulting beige coloured precipitate was filtered under vacuum, washed several times with petrol and ether, and then air dried,

to yield the product (28) (0.30g, 0.82mmol., Yield = 76%). The crude product was used in subsequent reactions without further purification.



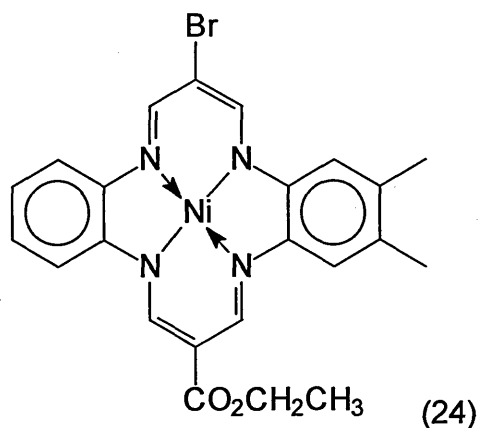
Mass Spectra	366	[M] ⁺
	287	[M-Br] ⁺
	277/241/213/119	

Stage 5 A solution of nickel(II) acetate tetrahydrate (0.3g, 1.2mmol.) in methanol (10ml.) was poured into a solution of the bis-anil (28) (0.4g, 1.1mmol.) in methanol (10ml.). The mixture was stirred for ½ hour, during which time a bright red solid formed. This was filtered under vacuum and washed several times with methanol before being air dried. The orange/red powder (29) (0.25g, 0.59mmol., Yield = 54%) was shown to be pure by TLC.



¹ H NMR spectra	δ 1.3	t, 3H
Solvent - CDCl ₃	δ 4.3	q, 2H
	δ 7.1-7.7	m, 4H
	δ 8.3	s, 2H
Mass Spectra	422	[M] ⁺
	350/211/183/155/58	
Microanalysis	<u>Theory</u>	<u>Found</u>
Calculated for	C 42.30%	C 41.33%
C ₁₅ H ₁₃ N ₂ O ₄ BrNi	H 3.09%	H 3.21%
	N 6.61%	N 6.25%

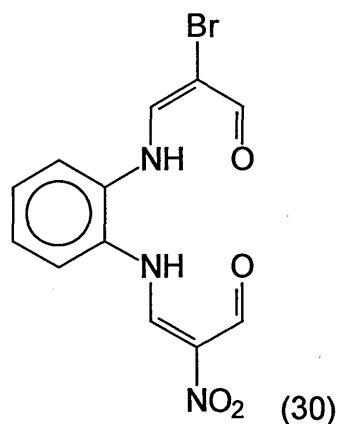
Stage 6 The nickel complex (29) (0.25g, 0.59mmol.) was mixed thoroughly with 4,5-dimethyl-ortho-phenylenediamine (0.25g, 1.4mmol.), and then heated to 130-140°C under nitrogen for 2 hours. The resulting dark brown solid was allowed to cool before ethanol was added, and the solid mass was broken up into a powdered form. The solid was filtered under vacuum, washed with ethanol, and air dried. The product was passed through a short silica gel column by elution with ethyl acetate/petrol/chloroform (20/30/50). Evaporation afforded the pure product as a brown powder (24) (0.20g, 0.38mmol., Yield = 65%).



Melting point	>300°C	
¹ H NMR spectra	δ 1.3	t, 3H
Solvent - CDCl ₃	δ 2.0	s, 6H
	δ 4.2	q, 2H
	δ 7.2	m, 6H
Mass Spectra	522/524	[M] ⁺ - Bromine isotopes
	494	[M-CH ₂ =CH ₂] ⁺ , McLafferty rearrangement
	444 - weak	[M-Br] ⁺
	416/108/44	
Microanalysis	<u>Theory</u>	<u>Found</u>
Calculated for C ₂₃ H ₂₁ N ₄ O ₂ NiBr	C 52.71%	C 53.80%
	H 4.04%	H 4.24%
	N 10.69%	N 10.76%
	Br 15.24%	Br 14.68%

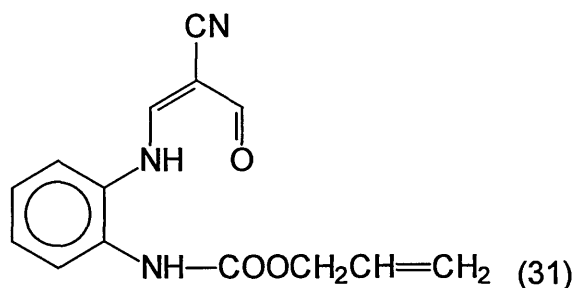
3.25 Preparation of alternative anils and reaction intermediates for the formation of 2-D unsymmetrical macrocyclic complexes of nickel (II)

In an attempt to synthesise the molecule illustrated (30), the sodium salt of 2-nitromalondialdehyde (7) (0.7g, 5mmol.), glacial acetic acid (1ml.) and dry tetrahydrofuran (20ml.) were placed in a 50ml. round bottom flask fitted with a pressure equalising dropping funnel. The mono-anil (27) (0.24g, 1mmol.) was dissolved in dry tetrahydrofuran (10ml.) and placed in the dropping funnel. The reagents were brought to reflux under nitrogen before the mono-anil was added dropwise. Heating was continued for three hours before being allowed to cool and added dropwise, with stirring into petrol. The resulting precipitate was filtered by vacuum, washed several times with ether and petrol, and then allowed to air dry to yield a brown solid (0.82g, 2.4mmol., Yield = 48%).



Infra-red spectra	3560cm ⁻¹ , 3490cm ⁻¹ and 3420cm ⁻¹	N-H str. - primary amine
	1640cm ⁻¹ and 1620cm ⁻¹	C=O str.

Synthesis of the mono-protected mono-anil (31) was attempted by condensation of the allyloxycarbonyl protected ortho-phenylenediamine (25) with 2-cyanomalondialdehyde† (3).



† 2-Cyanomalondialdehyde was triturated under petrol prior to use to yield a beige solid, which was air dried.

Method 1 Mono-protected ortho-phenylenediamine (25) (0.3g, 1.56mmol.) and a catalytic quantity of para-toluenesulphonic acid was dissolved in dry tetrahydrofuran (10ml.) and placed in a 50ml. 3-necked round bottom flask fitted with a reflux condenser and pressure equalising dropping funnel. 2-Cyanomalondialdehyde (3) (0.15g, 1.56mmol.) was dissolved in dry tetrahydrofuran (10ml.) and placed in the dropping funnel. The contents of the flask were brought to reflux under nitrogen before the malondialdehyde was added dropwise and the solution refluxed overnight. An orange solution was obtained which contained an orange precipitate. The solution was allowed to cool and the precipitate removed by filtration (0.11g). The orange filtrate was added with stirring into petrol (100ml.) resulting in the precipitation of an orange solid which was isolated by filtration (0.08g). Examination of the solids by TLC indicated that they consisted of mono-protected ortho-phenylenediamine (25) [positive test for amines when sprayed with iodo-platinic acid], and the required mono-protected mono-anil (31).

Mass spectra	271	[M] ⁺
	244	[M - CH=CH ₂] ⁺
	243/202	
	192	[Allyloxycarbonyl OPD] ⁺
	186	[M - COOCH ₂ CH=CH ₂] ⁺
	185/158/131/107	
	41	[CH ₂ CH=CH ₂] ⁺
Infra-red spectra	3600cm ⁻¹ -3200cm ⁻¹ broad	N-H str. - amines
	1710cm ⁻¹ (shoulder peak)	C=O str. - aldehydes
	1645cm ⁻¹	C=O str. - amides and/or
		C=C str. alkenes
	<u>Note</u> - absence of C-H str. - aldehyde, and C≡N str.	

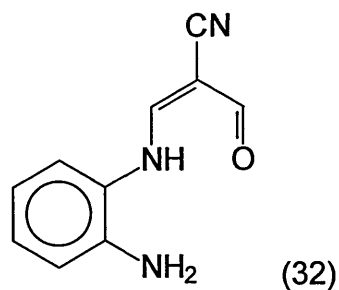
Method 2 Mono-protected ortho-phenylenediamine (25) (0.3g, 1.56mmol.) and a catalytic quantity of para-toluenesulphonic acid was dissolved in dry dimethylformamide (10ml.) and placed in a 50ml. 3-necked round bottom flask fitted with a reflux condenser and pressure equalising dropping funnel. 2-Cyanomalondialdehyde (3) (0.15g, 1.56mmol.) was dissolved in dry dimethylformamide (10ml.) and placed in the dropping funnel. The contents of the flask were brought to reflux under nitrogen before the malondialdehyde was added dropwise and the solution refluxed overnight. The solution was poured with stirring into petrol (100ml.), resulting in the formation of a beige precipitate which was isolated by filtration (0.32g, 1.2mmol. Yield = 77%).

Examination of the product by TLC showed a single spot at an R_f lower than that of the initial mono-protected ortho-phenylenediamine (25), and gave a negative response for amines when sprayed with iodo-platinic acid.

Mass spectra	271	[M] ⁺
	203	
	186	[M - COOCH ₂ CH=CH ₂] ⁺
	185/159/157/156/119	
	41	[CH ₂ CH=CH ₂] ⁺
Infra-red spectra	3250cm ⁻¹	N-H str. - 2° amine or amide
	2200cm ⁻¹	C≡N str. - nitrile
	1700cm ⁻¹	C=O str. - aldehyde
	1650cm ⁻¹	C=O str. - amide
	1620cm ⁻¹	C=C str. - aliphatic alkene
	1600cm ⁻¹ , 1580cm ⁻¹ and	C=C str. - aromatic and/or N-
	1520cm ⁻¹	H bend - amide

The mono anil (32) was prepared, as might be expected, by the deprotection of the mono-protected mono-anil (31).

A mixture of the allyloxycarbonyl protected mono-anil (31) (0.17g, 0.62mmol.), triphenylphosphine (0.066g, 0.25mmol.) and tetrakis (triphenylphosphine) palladium (0) (0.015g) was stirred in dry ether (2ml.). To this was added 2-ethylhexanoic acid (0.22g, 1.52mmol.) in dry ether (1ml.) and the mixture was stirred under nitrogen, in the dark for one hour. Examination of the mixture by TLC led to the identification of the product spot (positive test for amines when sprayed with para-(dimethylamino)benzaldehyde [Ehrlichs reagent]. The crude mixture was purified by column chromatography on silica gel with ethyl acetate/petrol/chloroform (20:30:50) as the eluant. Evaporation of the solvent led to the isolation of an orange solid (37mg, 0.20mmol., Yield = 32%).



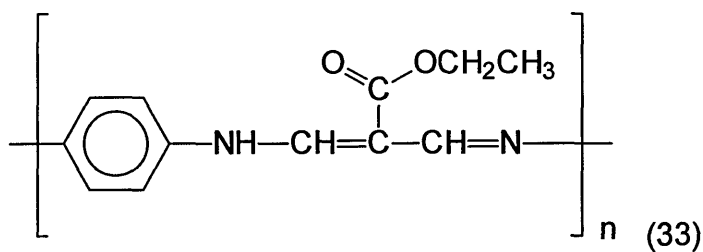
Mass spectra	278	$[\text{Ph}_3\text{P}=\text{O}]^+$
	277	
	262	$[\text{Ph}_3\text{P}]^+$
	158	$[\text{M} - \text{CHO}]^+$
	131/69	
Infra-red spectra	3380cm^{-1} and 3320cm^{-1}	N-H str. - amines

Polymeric Schiff bases

3.26 Schiff base polymer from 2-carboethoxymalondialdehyde and para-phenylenediamine

(33)

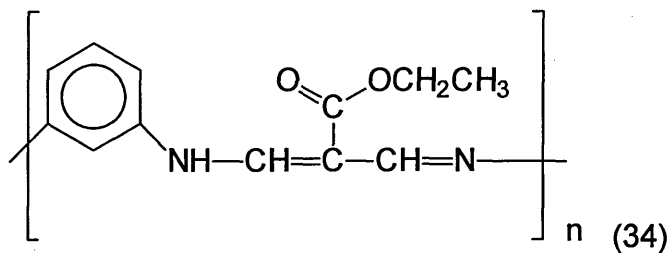
2-Carboethoxymalondialdehyde (2) (1.0g, 7mmol.) was placed in a three necked round bottom flask and dissolved in tetrahydrofuran (10ml.). To this was added a catalytic quantity of para-toluenesulphonic acid and the solution brought to reflux under nitrogen. Para-phenylenediamine (0.75g, 7mmol.) was dissolved in tetrahydrofuran (7ml.) and added to the reaction mixture via a pressure equalising dropping funnel. The solution was refluxed for one hour after which time the solution was cooled and the precipitated solid isolated by vacuum filtration. The crude solid was purified by soxhlet extraction with dichloromethane for 24 hours, after which the product was removed and air dried (0.73g).



Melting point	>340°C	
Infra-red spectra	3450cm ⁻¹	N-H stretch
	1690cm ⁻¹	C=O stretch
	1630cm ⁻¹	C=N stretch

3.27 Schiff base polymer from 2-carboethoxymalondialdehyde and meta-phenylenediamine

(34)



Method 1 2-Carboethoxymalondialdehyde (2) (1.0g, 7mmol.) was placed in a three necked round bottom flask and dissolved in tetrahydrofuran (10ml.). To this was added a catalytic quantity of para-toluenesulphonic acid and the solution brought to reflux under nitrogen. Meta-phenylenediamine (0.75g, 7mmol.) was dissolved in tetrahydrofuran (7ml.) and added to the reaction mixture via a pressure equalising dropping funnel. The solution was refluxed for one hour after which time the solution was cooled and the precipitated solid isolated by vacuum filtration. The crude solid was

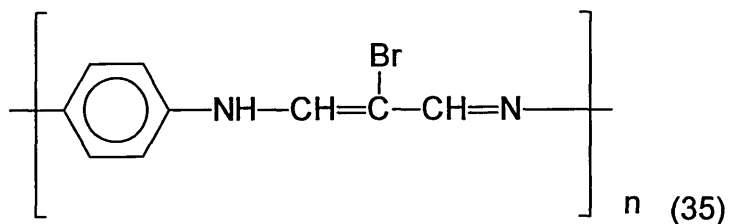
purified by soxhlet extraction with dichloromethane for 24 hours, after which the product was removed and air dried (0.40g).

Melting point	231-234°C	
Infra-red spectra	3440cm ⁻¹	N-H stretch
	2965cm ⁻¹	C-H stretch
	1630cm ⁻¹	C=C stretch
	1595cm ⁻¹	C=C stretch (aromatics)

Method 2 Meta-phenylenediamine (0.75g, 7mmol.) was dissolved in dry dimethylformamide (20ml.) along with a catalytic quantity of lithium chloride. to this was added 2-carboethoxymalondialdehyde (2) (1.0g, 7mmol.) in dry dimethylformamide (10ml.). The reaction mixture was stirred for 24 hours ,under nitrogen, in the dark. Upon filtration of the of the solution a solid was obtained that was washed with water (1 × 30ml.) and methanol (2 × 30ml.) (0.08g).

Melting point	>340°C	
Infra-red spectra	3440cm ⁻¹	N-H stretch
	2965cm ⁻¹	C-H stretch
	1630cm ⁻¹	C=C stretch
	1595cm ⁻¹	C=C stretch (aromatics)

3.28 Schiff base polymer from 2-bromomalondialdehyde and para-phenylenediamine (35)



2-Bromomalondialdehyde (8) (1.0g, 6.6mmol.) was placed in a three necked round bottom flask and dissolved in tetrahydrofuran (10ml.). To this was added a catalytic quantity of para-toluenesulphonic acid and the solution brought to reflux under nitrogen. Para-phenylenediamine (0.71g, 6.6mmol.) was dissolved in tetrahydrofuran (7ml.) and added to the reaction mixture via a pressure equalising dropping funnel. The solution was refluxed for one hour after which time the solution was cooled and the precipitated solid isolated by vacuum filtration. The crude solid was purified by soxhlet extraction with dichloromethane for 24 hours, after which the product was removed and air dried (1.18g).

Melting point

>340°C

Infra-red spectra

3460cm⁻¹

N-H stretch

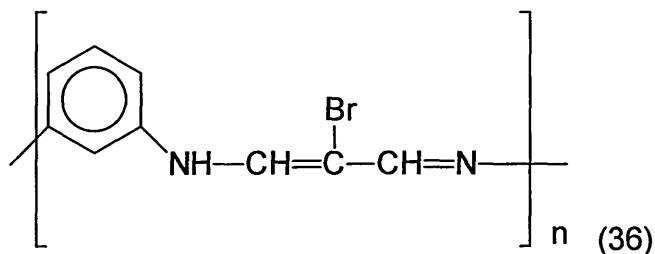
1615cm⁻¹

C=O stretch

1585cm⁻¹

C=O stretch

3.29 Schiff base polymers from 2-bromomalondialdehyde and meta-phenylenediamine (36)

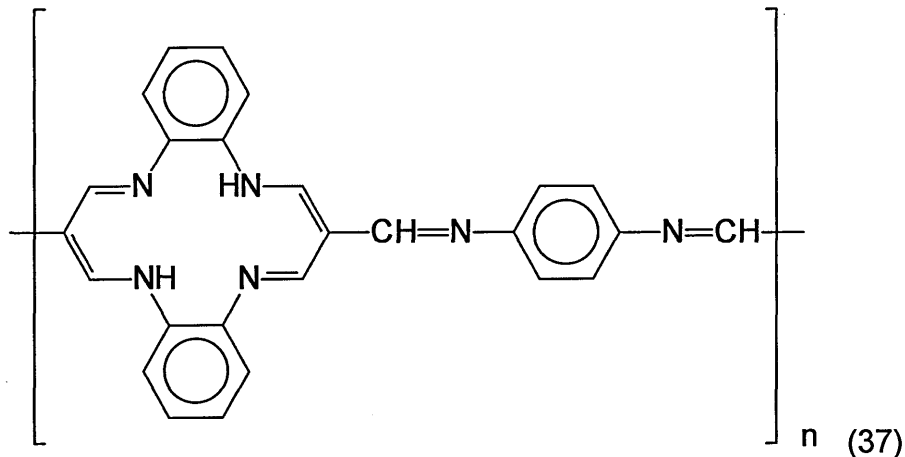


2-Bromomalondialdehyde (8) (1.0g, 6.6mmol.) was placed in a three necked round bottom flask and dissolved in tetrahydrofuran (10ml.). To this was added a catalytic quantity of para-toluenesulphonic acid and the solution brought to reflux under nitrogen. Meta-phenylenediamine (0.71g, 6.6mmol.) was dissolved in tetrahydrofuran (7ml.) and added to the reaction mixture via a pressure equalising dropping funnel. The solution was refluxed for one hour after which time the solution was cooled and the precipitated solid isolated by vacuum filtration. The crude solid was purified by soxhlet extraction with dichloromethane for 24 hours, after which the product was removed and air dried (0.95g).

Melting point	>340°C	
Infra-red spectra	3460cm ⁻¹	N-H stretch
	1615cm ⁻¹	C=O stretch
	1585cm ⁻¹	C=O stretch

3.30 Polymer from the Schiff base condensation of 6,13-diformyldihydrodibenzo[b,i]

[1,4,8,11]tetraazacyclotetradecine and para-phenylenediamine (37)



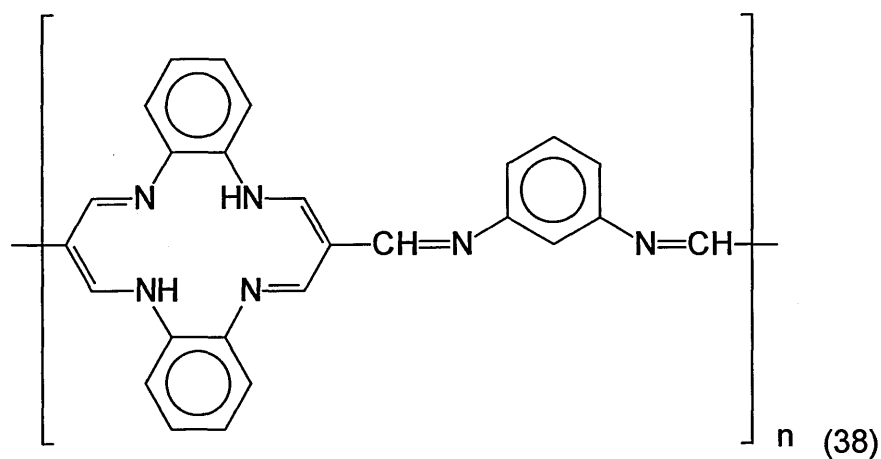
6,13-diformyldihydrodibenzo[b,i][1,4,8,11]tetraazacyclotetradecine (14) (0.26g, 0.8 mmol.) and a catalytic quantity of para-toluenesulphonic acid, were suspended in tetrahydrofuran (10ml.) in a 100ml. 3-necked round bottom flask. The solution was brought to reflux under nitrogen, at which time para-phenylenediamine (0.08g, 0.8mmol.) in tetrahydrofuran (10ml.) was added via a dropping funnel. The mixture was refluxed for one hour after which the reaction mixture was cooled and the precipitate was filtered off. Purification of the material by soxhlet extraction allowed the isolation of a red/brown solid (0.23g).

Melting point	>340°C	
Infra-red spectra	3420cm ⁻¹	N-H stretch
	3020cm ⁻¹	C-H stretch
	1610cm ⁻¹	C=C stretch
	1565cm ⁻¹	N-H bend
	1460cm ⁻¹	C-H bend
	1375cm ⁻¹	C-H bend

3.31 Polymers from the Schiff base condensation of 6,13-diformyldihydrodibenzo[b,i]

[1,4,8,11]tetraazacyclotetradecine and meta-phenylenediamine (38)

6,13-diformyldihydrodibenzo[b,i][1,4,8,11]tetraazacyclotetradecine (14) (0.45g, 1.3 mmol.) and a catalytic quantity of para-toluenesulphonic acid, were suspended in tetrahydrofuran (10ml.) in a 100ml. 3-necked round bottom flask. The solution was brought to reflux under nitrogen, at which time meta-phenylenediamine (0.14g, 1.3mmol.) in tetrahydrofuran (10ml.) was added via a dropping funnel. The mixture was refluxed for one hour after which the reaction mixture was cooled and the precipitate was filtered off. Purification of the material by soxhlet extraction allowed the isolation of a red/brown solid (0.30g).



Melting point

>340°C

Infra-red spectra

3460cm⁻¹

N-H stretch

3000cm⁻¹

C-H stretch

1610cm⁻¹

C=C stretch

1570cm⁻¹

N-H bend

1460cm⁻¹

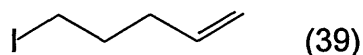
C-H bend

1375cm⁻¹

C-H bend

Preparation of quaternary phosphonium salts

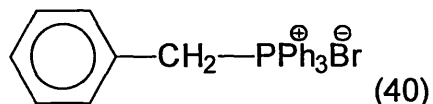
3.32 5-Iodo-1-pentene (39)



5-Chloro-1-pentene (1g, 0.01mol.) was placed in a 50ml. round bottom flask and dissolved in dry acetone (10ml.). the solution was brought to reflux under nitrogen before the addition of sodium iodide (1.43g, 0.01mol.) dissolved in dry acetone (10ml.). The resulting mixture was refluxed overnight under a nitrogen atmosphere, cooled, and then filtered to remove the NaCl precipitate. The acetone was removed by rotary evaporation to yield a yellow solid (1.96g, 0.01mol., Yield = 100%).

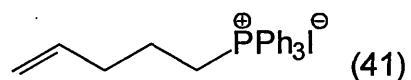
The product was found to be pure by TLC.

3.33 Benzyltriphenylphosphonium bromide (40)



Benzyl bromide (2.5g, 0.015mol.) was dissolved in dry toluene (10ml.) in a 50ml. round bottom flask and the mixture brought to reflux under nitrogen. To this was added triphenylphosphine (3.8g, 0.015mol.) in dry toluene (10ml.), and the whole was refluxed under nitrogen for 2 hours. The solution was cooled and the toluene evaporated. The remaining solid was added to dry ether (150ml.), stirred, and filtered before being allowed to air dry to yield a white solid (5.4g, 0.012mol., Yield = 83%). No data available

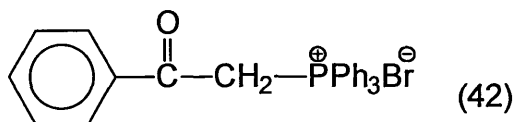
3.34 1-Pentenyl-5-triphenylphosphonium iodide (41)



5-Iodo-1-pentene (39) (1.96g, 0.01mol.) was dissolved in dry acetonitrile (20ml.) in a 50ml. round bottom flask. To this was added triphenylphosphine (2.6g, 0.01mol.) and the reaction mixture was refluxed overnight under a nitrogen atmosphere. After allowing to cool the acetonitrile was taken down to approximately 5ml. and then poured into dry ether (150ml.). The white precipitate formed was filtered and dried by suction (1.77g, 4mmol., Yield = 39%).

Mass spectra	332	[M+H-I] ⁺
Ionisation - FAB	277	
	185	
	93	
Infra-red spectra	3040cm ⁻¹	C-H stretch, aromatic
	2900cm ⁻¹	C-H stretch, aliphatic
	1670cm ⁻¹	C=C stretch, alkenes
	1495cm ⁻¹	C=C stretch, aromatics
	1450cm ⁻¹	C-H bend, aliphatics
	995cm ⁻¹	C-H bend, alkenes

3.35 Phenacyltriphenylphosphonium bromide (42)



Method 1 Triphenylphosphine (13g, 0.05mol.) and phenacyl bromide (9.95g, 0.05mol.) were dissolved in dry acetonitrile (40ml.) and refluxed under nitrogen for 1½ hours. After cooling, the reaction mixture was poured into ether (150ml.) and the precipitated solid filtered by suction and allowed to dry overnight (12.7g, 0.027mol., Yield = 55%).

³¹ P NMR Spectroscopy	δ 22	
Solvent CDCl ₃	δ 42	
Mass spectra	557	
Ionisation - FAB	381	[M] ⁺
	279	Base peak

Method 2²⁸⁸ Phenacyl bromide (8.35g, 0.04mol.) was added in portions to a stirred chloroform solution of triphenylphosphine (10.89g, 0.04mol.). After approximately 15-20 minutes a beige precipitate occurred and the reaction mixture was filtered into 1l. of dry ether to yield a precipitate that fumed on contact with the air and changed in appearance from a beige powder to a brown syrup. The product was not isolated. No data available.

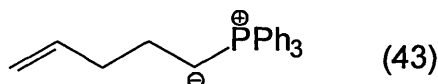
Method 3 Phenacyl bromide (8.35g, 0.04mol.) was dissolved in dichloromethane (35ml.) and was slowly added to a refluxing solution of triphenylphosphine (10.89g, 0.04mol.) in dichloromethane (40ml.). Upon continued refluxing for 20 mins. colour changes from khaki → amber → beige precipitate. The solution was cooled and the dichloromethane removed by rotary evaporation and the

isolated solid added to dry ether (500ml.) and then filtered to yield a beige solid (15.3g, 0.033mmol.,
 Yield = 83%, m.p. 295-299°C c.f. Lit. 269-271°C and 279-280°C - however the occurrence of different
 crystalline forms has been verified²⁸⁸ which is dependent upon the reaction conditions.

¹ H NMR spectroscopy	δ 3.3	s, 1H
Solvent - CD ₃ OD	δ 4.9	s, unknown
	δ 7.55	t*
	δ 7.7	m*
	δ 7.85	m*
	δ 8.1	d*
		*Total - 20H
³¹ P NMR spectroscopy	δ 22	
Solvent - CD ₃ OD		
Mass spectra	381	[M-Br] ⁺
Ionisation - FAB	185	[M-Br-C ₆ H ₅ CH ₂ O-C ₆ H ₅] ⁺
	93	

Preparation of phosphorous ylides

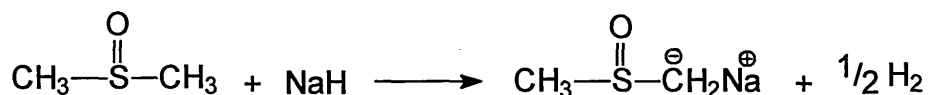
3.36 Phosphorous ylide of 1-pentenyl-5-triphenyl phosphonium iodide (43)



Method 1 The phosphonium salt, 1-pentenyl-5-triphenylphosphonium iodide (41) (1.5g, 3.3mmol.), was dissolved in dry tetrahydrofuran (20ml.) in a 50ml. round bottom flask, the mixture was stirred under nitrogen. To this was added n-butyl lithium (3.24ml. of 1.02M soln., 3.3mmol.) by syringe and the mixture was stirred for ½ hour. Material not isolated, used "as is" for reaction with aldehyde.

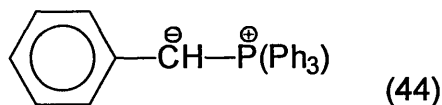
Method 2 1-Pentenyl-5-triphenylphosphonium iodide (41) (1.5g, 3.3mmol.) was placed in a 50ml. round bottom flask and dissolved in dry benzene (20ml.). The mixture was stirred under nitrogen while sodium hydride (0.08g, 3.3mmol.), after complete addition the reaction was stirred for a further 30 mins. Material not isolated, used "as is" for reaction with aldehyde.

Method 3 Dimethyl sulphoxide (50ml., 55.05g, 0.7mol.) was placed in a 250ml. round bottom flask and stirred under nitrogen. To this was added, in portions, sodium hydride (0.06g, 0.005mol.) to give a solution of dimethyl sodium (0.01M).



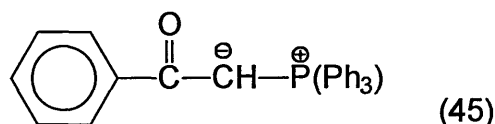
1-Pentenyl-5-triphenylphosphonium bromide (41) (0.33g, 0.7mmol.) was dissolved in dimethylsulphoxide (2ml.) and placed in a 100ml. 3-necked round bottom flask, fitted with a stirrer, septum, and 50ml. pressure equalising dropping funnel, under nitrogen. From a syringe was added dimethyl sodium (10ml. of 0.1M, 1mmol.) and the mixture stirred for ½ hour. Material not isolated, used "as is" for reaction with aldehyde.

3.37 Phosphorous ylide of benzyltriphenylphosphonium bromide (44)



In a 50ml. 3-necked round bottom flask fitted with a 50ml. pressure equalising dropping funnel, a septum and a stirrer bar was placed dry ethanol (10ml.). To this was added, in portions, sodium (0.11g, 4.6mmol.) and the apparatus flushed with nitrogen. From the dropping funnel was added benzyltriphenylphosphonium bromide (40) (2g, 0.46mmol.) dissolved in dry ethanol (10ml.). Stirring was continued for 30 mins. Material not isolated, used "as is" for reaction with aldehyde.

3.38 Phosphorous ylide of phenacyltriphenylphosphonium bromide (45)



To a 100ml. round bottom flask fitted with a stirrer was added phenacyltriphenylphosphonium bromide(42 - 3.35 method 1) (4g, 0.01mol.), ethanol (20ml.) and water (10ml.). To the reaction mixture was added a solution of sodium carbonate (2g, 0.02mol.) in water (10ml.). Stirring was continued for 60 mins. after which the solution was extracted with dichloromethane (3 × 50ml.), dried (MgSO₄), and evaporated to give the ylide as a viscous orange liquid (2.57g, 7mmol.). The liquid was scratched under dry ether to yield the product as an off white powder (2.57g, 7mmol., Yield = 70%)

Melting point	179-181°C	Literature : 179-180°C
³¹ P NMR spectroscopy	δ 17	
Solvent - CDCl ₃	δ 29	
Mass spectra	381	[M+H] ⁺
Ionisation - FAB	279	
	185	[M-C ₆ H ₅ CH ₂ O-C ₆ H ₅] ⁺
	93	

The above procedure was repeated with the phenacyltriphenylphosphonium bromide (42) isolated from 3.35 method 3 and gave slightly different results. The material was evaporated under reduced pressure to yield a viscous solid/liquid mix that expanded during evaporation. The material was triturated under dry ether and filtered to yield a pale beige product (2.8g, 7.6mmol., Yield = 76.3%.)

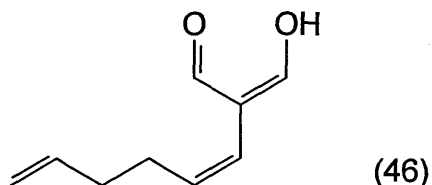
Melting point	179-181°C	Literature : 179-180°C
¹ H NMR spectroscopy	δ 3.3	s, 1H
Solvent - CD ₃ OD	δ 4.9	s, unknown
	δ 7.35	m*
	δ 7.65	m*
	δ 7.9	m*
		*Total 20H
³¹ P NMR spectroscopy	δ 16.5	
Solvent - CDCl ₃		

Mass spectra	381	[M+H] ⁺
Ionisation - FAB	279	
	185	[M-C ₆ H ₅ CH ₂ O-C ₆ H ₅] ⁺
	93	

Reaction of carbonyl compounds with phosphorous ylides

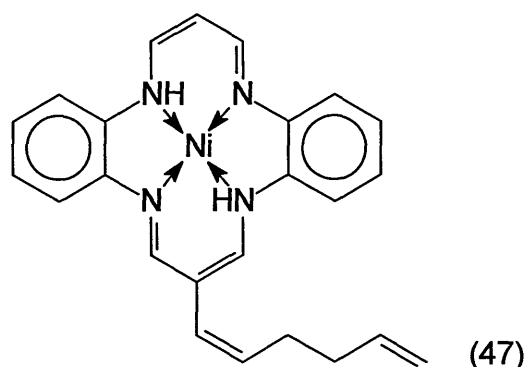
3.38 2-(1,5-Hexadiene)malondialdehyde (46)

Method 1 To the tetrahydrofuran solution containing the 1-pentenyl-5-triphenylphosphonium ylide (43) (3.36 Method 1), was added triformylmethane (5) (0.33g, 3.3mmol.) in dry tetrahydrofuran (5ml.). The reaction mixture was stirred under nitrogen for 1 hour. TLC (10% ethanol in dichloromethane) at this stage showed the presence of a new spot and the disappearance of the spot due to the phosphonium salt. Solvent extraction with dichloromethane and water (3 × 50ml.) was attempted, however, TLC showed that the reliberation of the phosphonium salt had occurred.



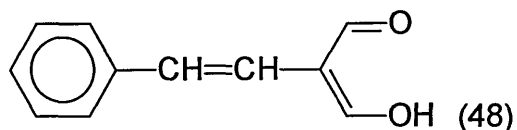
Method 2 To the benzene solution containing the 1-pentenyl-5-triphenylphosphonium ylide (Sect. 3.36 Method 2), was added triformylmethane (5) (0.33g, 3.3mmol.) in dry benzene (10ml.). The flask was stirred under nitrogen for 1 hour, with a yellow colouration being observed after 30 mins. The reaction mixture was filtered and a TLC study performed (10% ethanol in dichloromethane) which showed the presence of a new spot, which was assumed to be the required product. Isolation of pure product could not be attained.

3.40 6-(1,5-Hexadiene)dihydrodibenzo[b,i][1,4,8,11]tetraazacyclotetra decine nickel(II) (47)



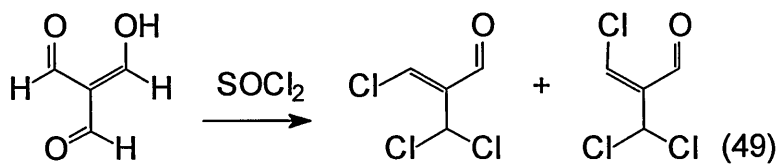
To the dimethylsulphoxide solution of 1-pentenyl-5-triphenylphosphonium ylide (section 3.36 method 3), was added 6-formyl-dihydrodibenzo[b,i][1,4,8,11] tetra azacyclotetradecine nickel(II) (0.27g, 0.7mmol.) dissolved in dimethylsulphoxide (10ml.). The flask was stirred under nitrogen for 1 hour and the product isolated by evaporation under reduced pressure (0.55g). Mass spectral data showed the material to be predominately the macrocycle containing the formyl functionality, $[M]^+ = 372$

3.41 2-(2-Phenylethyl-1-ene)malondialdehyde (48)



To the ethanolic solution of benzyltriphenylphosphonium ylide (44) was added triformylmethane (5) (0.46g, 4.6mmol.) dissolved in dry ethanol (5ml.) with stirring. The solution was stirred for 1 hour and the reaction mixture studied by TLC (10% ethanol in dichloromethane), which showed an additional spot to be present in addition to the expected triphenylphosphine oxide (a side product of the Wittig reaction).

3.42 3-chloro-2-(dichloromethyl)propenal²⁷⁷ (49)



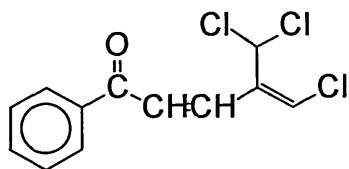
Triformylmethane (5) (1g, 0.01mol.) was added, with stirring and cooling (with an ice bath), to excess thionyl chloride (7ml.). The mixture was stirred overnight at room temperature and then heated to 60°C for 1 hour. Excess thionyl chloride was removed under reduced pressure and the product (mixture of E and Z isomers) was isolated by distillation (1.18g, 6.8mmol., Yield = 68%)

Mass spectra	195/193/191		
	176/174/172	[M] ⁺	
	141/139/137	[M-Cl] ⁺	
	110/108	[M-ClCHCl] ⁺	
	90		
	73		
¹ H NMR spectra	δ 3.05	d, 1H	
	Solvent - CDCl ₃	δ 6.6	d, 2H
		δ 6.85	s, 3H
		δ 7.05	s, 1H
		δ 7.3	s, 2H
		δ 7.9	s, 1H
		δ 9.6	s, 2H
		δ 10.1	s, 1H

3.43 Reaction of phenacyltriphenylphosphonium ylide with 3-chloro-2-(dichloromethyl)propenal

propenal²⁷⁷ (50)

Method 1 Phenacyltriphenylphosphonium ylide (45) (1.3g, 3.5mmol.) [isolated from the phosphonium salt prepared as described in section 3.35 method 1] in dry tetrahydrofuran (10ml.) was placed into a 100ml round bottom flask and stirred. to the solution was added 3-chloro-2-(dichloromethyl)propenal (0.5g, 3mmol.) (49) which immediately resulted in the production of an orange colouration. The reaction mixture was stirred for 30 minutes and then monitored by TLC (10% ethanol in dichloromethane) which illustrated the presence of a product spot in addition to a spot with the same R_f as triphenylphosphine oxide and the starting ylide. The solution was filtered to yield an orange solid (0.35g), the filtrate was poured into excess ether with stirring which resulted in the isolation of further orange solid (0.5g) which gave the same results by TLC but also showed a slight impurity. The purification of the material was attempted by flash chromatography (10% ethanol in dichloromethane), but the procedure yielded material that was slightly contaminated (0.41g, 1.5mmol., Yield = 50%).



plus isomers (50)

Mass spectra	379	[Phosphorous ylide] ⁺ = X
Ionisation - EI	303	[X-Ph] ⁺
	277 - Chlorine isotope	[M] ⁺
	262	[PPh ₃] ⁺
	201/183/152/108	
	77	[Ph] ⁺

Mass spectra	381	[Phosphorous ylide] ⁺ = X
Ionisation - FAB	303	[X-Ph] ⁺
	279/275	[M] ⁺
	201/185	
	105	[PhCO] ⁺
	93	
³¹ P NMR spectroscopy	δ 21.7	
Solvent - CDCl ₃	δ 29.4 - extremely faint	

Method 2 To the phenacyltriphenylphosphonium ylide (45) (1.3g, 3.5mmol.) [isolated from the phosphonium salt prepared as described in section 3.35 method 3] in dry dichloromethane (10ml.) was added to a 100ml. round bottom flask containing 3-chloro-2-(dichloromethyl)propenal (49) (0.5g, 3mmol.) dissolved in dry dichloromethane (10ml.). The reaction mixture was then stirred overnight under nitrogen, resulting in the formation of a bright orange solution. A TLC study of the solution was performed (10% ethanol in dichloromethane). The dichloromethane was taken down to 5ml. after which the solution was poured with stirring into excess ether (300ml.) to yield a bright orange crystalline product (1.5g). Examination of the material by TLC (10% ethanol in dichloromethane) illustrated the presence of a product spot with the same R_f as the phosphonium ylide which showed a negative response to dinitrophenylhydrazine.

Mass spectra	379
	302
	277
	183
	152
	108

^{31}P NMR spectroscopy δ 21.6

Solvent - CDCl_3 δ 28.6

^1H NMR spectroscopy δ 6.3

Solvent - CDCl_3 δ 7.4 - 8.0 Aromatics

δ 8.3

δ 9.2

δ 9.8 br s, Aldehyde

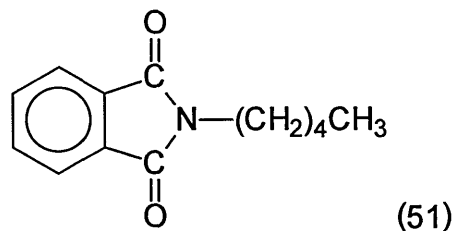
Numerous smaller peaks at δ

1.25, 3.0, 5.3, 6.55, 6.8, 7.0,

7.25

The Gabriel synthesis of amines²⁷²

3.44 N-Pentylphthalimide (51)



Potassium phthalimide (5g, 0.027mol.) was added to a solution of 1-bromopentane (4.0g, 0.027mol) in dimethylformamide (20ml.), in a 100ml. round bottom flask. The flask was stirred and heated by a hotplate until hot to the touch. The heat was removed and the mixture heated for a further 30 minutes. The solution was cooled before chloroform (30ml.) was added, and the solution transferred to a separating funnel containing water (100ml.). The aqueous phase was extracted with chloroform (2 × 10ml.). The chloroform extracts were combined before being washed with NaOH (20ml., 2M) and

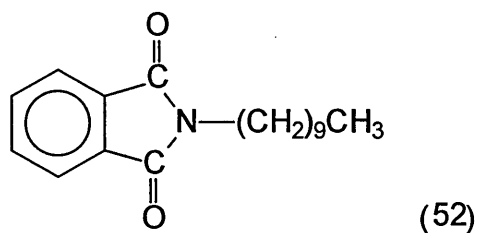
then water (20ml.). The chloroform solution was dried with MgSO_4 and then evaporated under reduced pressure to give a clear yellow liquid (5.14g, 0.024mol., Yield = 88%).

Mass spectra	217	$[\text{M}]^+$
	160	$[\text{M}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3]^+$
	73	$[\text{DMF}]^+$
	57	$[\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3]^+$
	43	$[\text{CH}_2\text{CH}_2\text{CH}_3]^+$
^1H NMR spectroscopy	δ 0.8	t, 3H - CH_3 -
Solvent - CDCl_3	δ 1.25	m, 4H - $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$
	δ 1.6	q, 2H - $(\text{CH}_2)_2\text{CH}_2\text{CH}_2\text{N}$
	δ 2.8	d - DMF
	δ 4.6	t, 2H - $\text{CH}_2\text{CH}_2\text{N}$
	δ 7.65	m, 2H- Aryl H
	δ 7.75	m, 2H- Aryl H
	δ 7.95	s- DMF

The yellow liquid was redissolved in chloroform (10ml.) and placed in a 100ml separating funnel. In an attempt to remove the residual dimethylformamide the solution was then washed with saturated brine ($3 \times 40\text{ml.}$) before being dried with MgSO_4 and evaporated under reduced pressure to yield a clear yellow liquid (5.0g, 0.023mol., Yield = 85%).

^1H NMR spectroscopy	δ 0.8	t, 3H - CH_3 -
Solvent - CDCl_3	δ 1.25	m, 4H - $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$
	δ 1.6	q, 2H - $(\text{CH}_2)_2\text{CH}_2\text{CH}_2\text{N}$
	δ 4.6	t, 2H - $\text{CH}_2\text{CH}_2\text{N}$
	δ 7.65	m, 2H- Aryl H
	δ 7.75	m, 2H- Aryl H

3.45 N-Decylphthalimide (52)

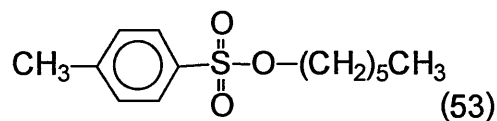


Potassium phthalimide (5g, 0.027mol.) was added to a solution of 1-bromodecane (5.9g, 0.027mol) in dimethylformamide (20ml.), in a 100ml. round bottom flask. The flask was stirred and heated by a hotplate until hot to the touch. The heat was removed and the mixture heated for a further 30 minutes. The solution was cooled before chloroform (30ml.) was added, and the solution transferred to a separating funnel containing water (100ml.). The aqueous phase was extracted with chloroform (2 \times 10ml.). The chloroform extracts were combined before being washed with NaOH (20ml., 2M) and then water (20ml.). The chloroform solution was then washed with saturated brine (3 \times 40ml.) before being dried with MgSO_4 and then evaporated under reduced pressure to give a clear yellow liquid which crystallised upon standing to give a white solid (6.0g, 0.021mol., Yield = 77%).

Mass spectra	287	$[\text{M}]^+$
	160	$[\text{M}-(\text{CH}_2)_8\text{CH}_3]^+$

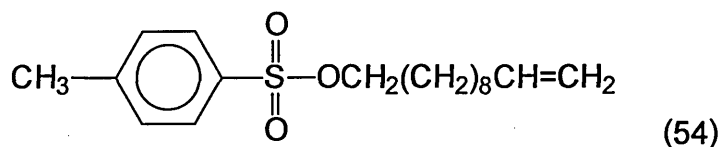
3.46 n-Hexyl para-toluenesulphonate (53)

Into a 100ml. round bottom flask was weighed 1-hexanol (5.11g, .05mol.), para-toluenesulphonyl chloride (10.5g, 0.55mol.) and pyridine (7.91g, 0.1mol.). To this was added dichloromethane (20ml) and the solution was stirred for 1 hour which resulted in the development of a precipitate of pyridinium hydrochloride. The precipitate was removed by filtration before the filtrate was transferred to a 100ml. separating funnel and washed with hydrochloric acid (3 × 50ml., 2M) and water (1 × 50ml.). Evaporation of the chloroform under reduced pressure resulted in the isolation of a clear liquid (9.47g, 0.037mol., Yield = 74%).



Mass spectra	256	[M] ⁺
	173	
	155	[M- O(CH ₂) ₅ CH ₃] ⁺
	91	[M-C ₆ H ₄ CH ₃] ⁺
	84	

3.47 10-undecenyl para-toluenesulphonate (54)

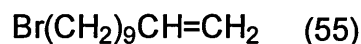


10-Undecen-1-ol (8.5g, 0.05mol.), para-toluenesulphonyl chloride (10.5g, 0.055mol.) and pyridine (4.7g, 0.06mol.) were dissolved in dichloromethane (20ml.) in a 100ml. round bottom flask. The

reaction mixture was stirred overnight. Pyridine was removed by solvent extraction with HCl (2M, 3 × 40ml.) and water (1 × 40ml.). The dichloromethane layer was dried (MgSO₄) and evaporated under reduced pressure to yield the crude product (9.1g). This was purified on a silica column (ethyl acetate/petrol 30:70) to isolate the product as a colourless liquid (5.4g, 0.02mol., Yield = 35%).

Mass spectra	368/256	
	185	[M-(CH ₂) ₈ CH=CH ₂] ⁺
	171	[M-(CH ₂) ₉ CH=CH ₂] ⁺
	155	[M-O(CH ₂) ₉ CH=CH ₂] ⁺
	152	
	91	[CH ₃ C ₆ H ₄] ⁺
	68	
	55	[CH ₂ =CHCH ₂ CH ₂] ⁺

3.48 11-bromoundec-1-ene (55)



Method 1 10-undecenyl para-toluenesulphonate (54) (1.34g, 4mmol.) and sodium bromide (0.5g, 3mmol.) were placed in 50ml. round bottom flask and dissolved in dry tetrahydrofuran (10ml.). The reaction mixture was refluxed for 1 hour under nitrogen. The cooled solution was filtered to yield a milky white liquid (0.81g), this was refiltered through celite to yield the colourless product 11-bromoundec-1-ene (55) (0.6g, 2.6mmol., Yield = 65%).

Mass spectra	152	$[M-Br]^+$
	139 (weak)	$[M-CH_2Br]^+$
	97	$[M-(CH_2)_4Br]^+$
	91	
	83	$[M-(CH_2)_5Br]^+$
	69	$[M-(CH_2)_6Br]^+$
	55	$[M-(CH_2)_7Br]^+$
	41	$[M-(CH_2)_8Br]^+$

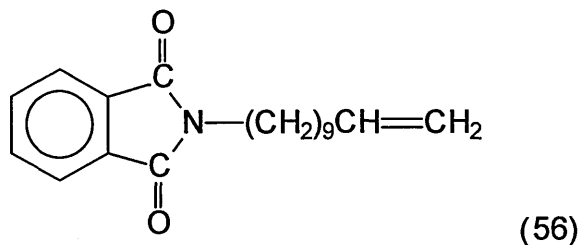
Method 2 10-undecenyl para-toluenesulphonate (54) (4.0g, 12mmol.) and tetra-n-butylammonium bromide (5g, 16mmol.) were placed in a 50ml. round bottom flask and dissolved in dry tetrahydrofuran (20ml.). The reaction mixture was refluxed under nitrogen for 1 hour. The tetrahydrofuran was removed under reduced pressure. N-butylammonium tosylate was removed from the sample by solvent extraction with water (1× 50ml.) and ether (4 × 50ml.). The ether layer was dried ($MgSO_4$) and evaporated to yield a slightly yellow liquid product of 11-bromoundec-1-ene (55) (2.5g, 11mmol., Yield = 89%).

Mass spectra	277/209/183/157/121/91	
	67	$[M-(CH_2)_6Br]^+$
	55	$[M-(CH_2)_7Br]^+$
	41	$[M-(CH_2)_8Br]^+$

^1H NMR spectroscopy	δ 1.35	Br s, 12H, R- <u>CH</u> ₂ -R
Solvent - CDCl_3	δ 1.85	quin, 2H, <u>CH</u> ₂ CH ₂ Br
	δ 2.05	quart, 2H, <u>CH</u> ₂ -CH=CH ₂
	δ 3.4	t, 2H, <u>CH</u> ₂ Br
	δ 4.95	t?, 2H, CH= <u>CH</u> ₂
	δ 5.8	m, 1H, <u>CH</u> =CH ₂

The material produced via both the above methods was found to give the same reaction products in subsequent reactions.

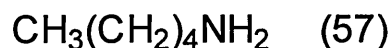
3.49 N-Undec-1-enylphthalimide (56)



11-Bromoundec-1-ene (55) (2.5g, 11mmol.) was dissolved in dimethylformamide (10ml.) and placed in a 50ml. round bottom flask. To this was added potassium phthalimide (2.0g, 11mmol.) and the flask was heated until hot to the touch. The heat was removed and the flask stirred for 30 mins. The solution was allowed to cool before adding chloroform (30ml.), and transferring the products to a separating funnel containing water (100ml.). The aqueous phase was extracted with chloroform (3 × 20ml.) and the resultant extracts combined. These combined extracts were washed with NaOH (2M, 20ml) and then water (20ml.). The chloroform was evaporated to 10ml. under reduced pressure and washed with saturated sodium chloride (3 × 40ml.) to remove excess dimethylformamide. The chloroform layer was dried (MgSO_4) and evaporated under reduced pressure to give a yellow liquid that solidified to an off-white powder (2.22g, 7.5mmol., Yield = 68%).

Mass spectra	299	$[M]^+$
	202	$[M-(CH_2)_5CH=CH_2]^+$
	188	$[M-(CH_2)_6CH=CH_2]^+$
	174	$[M-(CH_2)_7CH=CH_2]^+$
	160	$[M-(CH_2)_8CH=CH_2]^+$
	55	$[CH_2=CHCH_2CH_2]^+$
	41	$[CH_2=CHCH_2]^+$
1H NMR spectroscopy	δ 1.3	Br s, 12H, R- <u>CH</u> ₂ -R
Solvent - $CDCl_3$	δ 1.75	Br s, 2H, <u>CH</u> ₂ CH ₂ N
	δ 2.0	Quart, 2H, <u>CH</u> ₂ -CH=CH ₂
	δ 2.9	Dimethylformamide
	δ 3.65	t, 2H, <u>CH</u> ₂ N
	δ 4.95	t?, 2H, CH= <u>CH</u> ₂
	δ 5.8	m, 1H, <u>CH</u> =CH ₂
	δ 7.2	
	δ 7.8	m, 4H, Aryl-H
	δ 8.05	Dimethylformamide

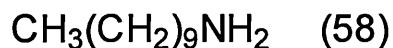
3.50 1-Pentamine (57)



N-pentylphthalimide (51) (2.14g, 0.01mol.), and hydrazine monohydrate (1.2ml., 0.02mol) were weighed into a 100ml round bottom flask fitted with a reflux condenser. The reagents were dissolved in methanol (50ml.) and the solution refluxed under nitrogen for 1 hour. The solution was cooled before standing overnight, during which a white solid was found to precipitate (1.5g). This was found to be the phthalhydrazide side product by mass spectrometry. No trace of the 1-pentamine (57) was found although the material had the characteristic odour of amines.

Mass spectra	162	$[\text{M}]^+$
	132	$[\text{M}-\text{NHNH}]^+$
	104	$[\text{M}-\text{NHNHC}=\text{O}]^+$
	76	C_6H_4
	50	$\text{H}_2\text{NNH}_2 \cdot \text{H}_2\text{O}$

3.51 1-Decylamine (58)



N-decylphthalimide (52) (2.87g, 0.01mol.) and hydrazine monohydrate (1.2ml., 0.02mol.) were weighed into a 100ml. round bottom flask fitted with a reflux condenser. The reagents were dissolved in methanol (50ml.) and refluxed under nitrogen for 1 hour. The solution was allowed to cool before standing overnight, resulting in the precipitation of a white solid which was isolated by filtration. Analysis by mass spectra showed this to be the phthalhydrazide side product.

Mass spectra	162	$[M]^+$
	132	$[M-NHNH]^+$
	104	$[M-NHNHC=O]^+$
	76	C_6H_4
	50	$H_2NNH_2.H_2O$

The methanol from the filtrate was removed by rotary evaporation to yield an off white solid (1.4g).

Mass spectral data showed the material to be a mixture of 1-decylamine (51) absorbed onto phthalhydrazide.

Mass spectra		
1-decylamine	157	$[M]^+$
	142	$[M-CH_3]^+$
	128	$[M-CH_2CH_3]^+$
	114	$[M-(CH_2)_2CH_3]^+$
	100	$[M-(CH_2)_3CH_3]^+$
	86	$[M-(CH_2)_4CH_3]^+$
	69	$[M-(CH_2)_5CH_3]^+$
	57	$[M-(CH_2)_6NH_2]^+$
	44	$[M-(CH_2)_7CH_3]^+$
Phthalhydrazide	162	$[M]^+$
	132	$[M-NHNH]^+$
	104	$[M-NHNHC=O]^+$
	76	C_6H_4
	50	$H_2NNH_2.H_2O$

Purification of the solid by soxhlet extraction with chloroform was found to be only partly effective since some of the phthalhydrazide was found to extract. Solvent extraction was attempted by washing the chloroform solution with 2M hydrochloric acid (1 × 100ml.). This resulted in the formation of a soapy aqueous phase which was difficult to separate. The mixture was made alkaline by the addition of NaOH which had the effect of removing the phthalhydrazide impurity. The chloroform was evaporated under reduced pressure to yield a clear liquid (0.45g, 2.9mmol., Yield = 29%).

Mass spectra	157	[M] ⁺
	100	[M-(CH ₂) ₃ CH ₃] ⁺
	86	[M-(CH ₂) ₄ CH ₃] ⁺
	69	[M-(CH ₂) ₅ CH ₃] ⁺
	44	[M-(CH ₂) ₇ CH ₃] ⁺
Infra red spectra	3305cm ⁻¹	N-H str.
	2885cm ⁻¹	C-H str. - aliphatic
	2820cm ⁻¹	C-H str. - aliphatic
	1550cm ⁻¹	N-H bend - primary amines
	1455cm ⁻¹	C-H bend - aliphatic

3.52 11-Aminoundec-1-ene (59)



N-undec-1-enyl-11-phthalimide (56) (2.22g, 7.5mmol.), methanol (30ml.) and hydrazine hydrate (1.2ml., 0.025mol.), were refluxed for 1 hour under nitrogen. After this time the heat was removed

and the mixture allowed to stand overnight which resulted in the formation of an abundance of white crystals. The methanol was removed under reduced pressure, and the solid was extracted, using a soxhlet apparatus, with petrol for 24 hours. The petrol was dried (MgSO_4) and evaporated to yield the desired 11-aminoundec-1-ene (52) as a pale yellow liquid (0.9g, 5.3mmol., 71%).

Mass spectra	169	$[\text{M}]^+$
	128	$[\text{M}-\text{CH}_2\text{CH}=\text{CH}_2]^+$
	112	$[\text{M}-(\text{CH}_2)_2\text{CH}=\text{CH}_2]^+$
	100	$[\text{M}-(\text{CH}_2)_3\text{CH}=\text{CH}_2]^+$
	86	$[\text{M}-(\text{CH}_2)_4\text{CH}=\text{CH}_2]^+$
	72	$[\text{M}-(\text{CH}_2)_5\text{CH}=\text{CH}_2]^+$
	69	$[\text{M}-(\text{CH}_2)_6\text{NH}_2]^+$
	55	$[\text{M}-(\text{CH}_2)_7\text{NH}_2]^+$
	44	$[\text{M}-(\text{CH}_2)_7\text{CH}=\text{CH}_2]^+$
41	$[\text{M}-(\text{CH}_2)_8\text{NH}_2]^+$	
Infra red spectra	3310cm^{-1}	N-H str.
	2885cm^{-1}	C-H str. - aliphatic
	2815cm^{-1}	C-H str. - aliphatic
	1620cm^{-1}	C=C str - alkenes
	1550cm^{-1}	N-H bend - primary amines
	$1455/1470\text{cm}^{-1}$	C-H bend - aliphatic

Chapter 6

Discussion

1. Introduction

The research undertaken may be broadly classified into four key areas:

1. The synthesis of existing and novel malondialdehydes.
2. The synthesis of both symmetrical and unsymmetrical macrocycles.
3. the preparation of linear Schiff base polymers.
4. The preparation of linear Schiff base polymers that incorporate macrocyclic units as part of the main chain and as pendant side chains.

This chapter is dedicated to the research in each of the above key areas.

2. Malondialdehydes

The use of malondialdehydes for the preparation of substituted dibenzotetraaza[14]annulenes has been well documented in the literature²⁸⁹⁻²⁹⁵. The development and use of the malondialdehydes has been of major importance in our attempt to develop novel macrocyclic and polymeric species, they are ideal for our purpose due to the nature of the dual aldehyde functionalities.

The general structure for a substituted malondialdehyde is shown below (Fig. 2.1), and illustrates the keto-enol tautomerism that exists within the molecule²⁹⁶. The enol form of malondialdehyde is the simplest example of a compound with a strong intramolecular hydrogen bond that leads to the formation of a delocalised chelate.

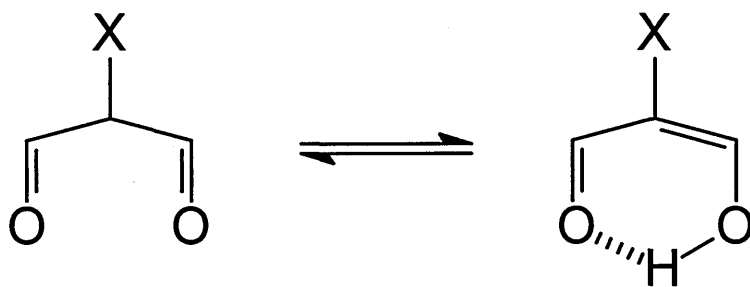


Fig. 2.1 Keto-enol tautomerism exhibited by substituted malondialdehydes.

Procedures documented in the literature²⁹⁷⁻³⁰⁵, and modifications based upon them, have allowed an extensive series of malondialdehydes to be prepared (Fig. 2.2).

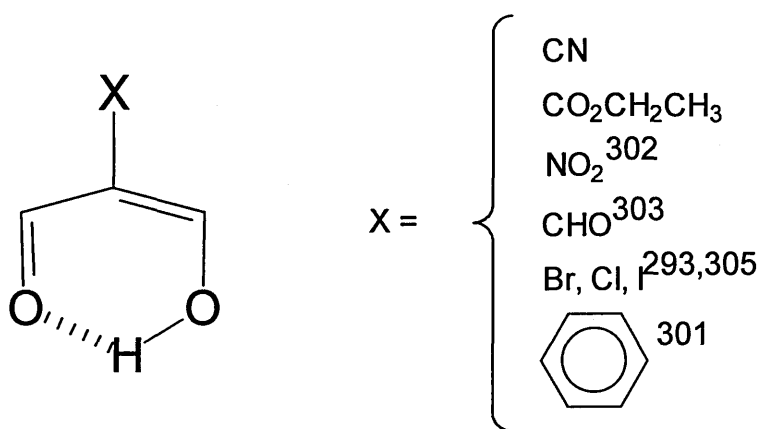


Fig. 2.2 Substituted malondialdehydes.

Due to the reactive nature of the malondialdehydes, it has proved necessary in some cases to store them as acetals. The acetal protection has also led to the synthesis of new substituted malondialdehydes and allowed the development of novel macrocycles and polymeric species that vary in the electronic properties they exhibit.

The established literature procedures were followed for the preparation of most malondialdehydes, however, in some cases modifications were required.

2.1 Preparation of 2-carboethoxymalondialdehyde (2).

The preparation of 2-carboethoxymalondialdehyde was initially achieved by the use of our own modification of the Reformatsky reaction³⁰⁶, and subsequent employment of the Pannizi reaction to yield the dialdehyde. The modified Reformatsky procedure (Fig. 2.3) utilises the reaction between ethyl bromoacetate and triethylorthoformate in the presence of an activated zinc catalyst to give the acetal-ester, ethyl 3,3-diethoxypropionate (1), as well as a by-product. Upon spectroscopic examination by NMR, the by-product appears to be an enol-ether that is formed by a thermal elimination reaction catalysed by the zinc derived Lewis acid species present.

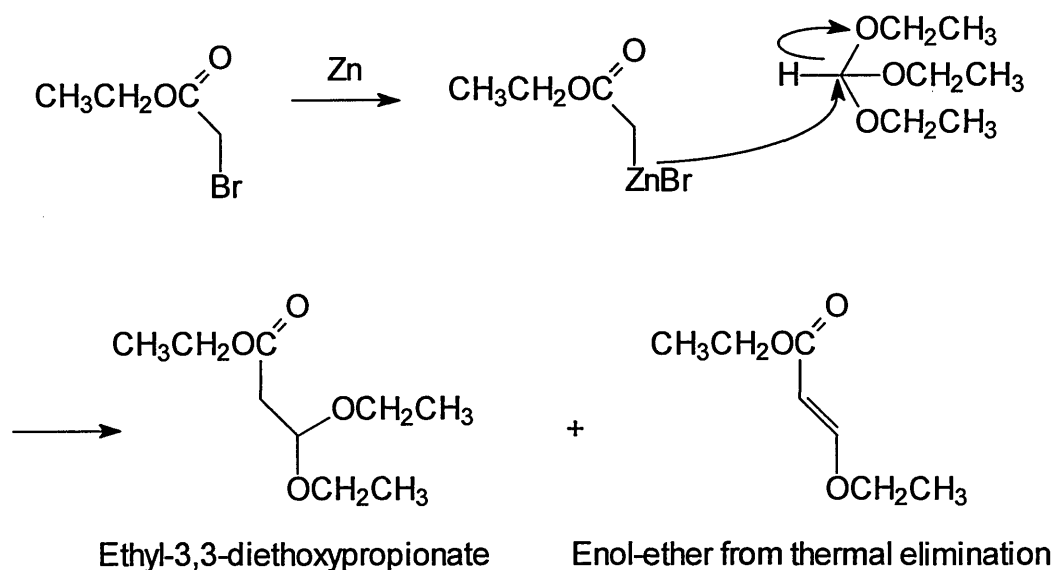


Fig. 2.3 Reformatsky formation of ethyl-3,3-diethoxypropionate.

Assessment of the product purity by gas chromatography showed that at best the molar ratio of ethyl 3,3-diethoxypropionate to enol-ether was 4:1. This ratio was reduced when the reaction temperature was increased by using toluene as the reflux solvent in place of benzene, as might be expected for a thermal elimination reaction.

Reaction of the Reformatsky product with sodium and ethyl formate, the Pannizi reaction, enabled the isolation of the 2-carboethoxymalondialdehyde upon acidification and extraction (Fig. 2.4). The

Pannizi reaction is a crossed Claisen ester condensation (i.e. involves two different esters) in which the electrophile is ethyl formate. The presence of the enol-ether does not appear to interfere with the formation of the malondialdehyde and the reaction mixture obtained is purified by capillary air bleed vacuum distillation to yield the pure 2-carboethoxymalondialdehyde as a pale yellow liquid.

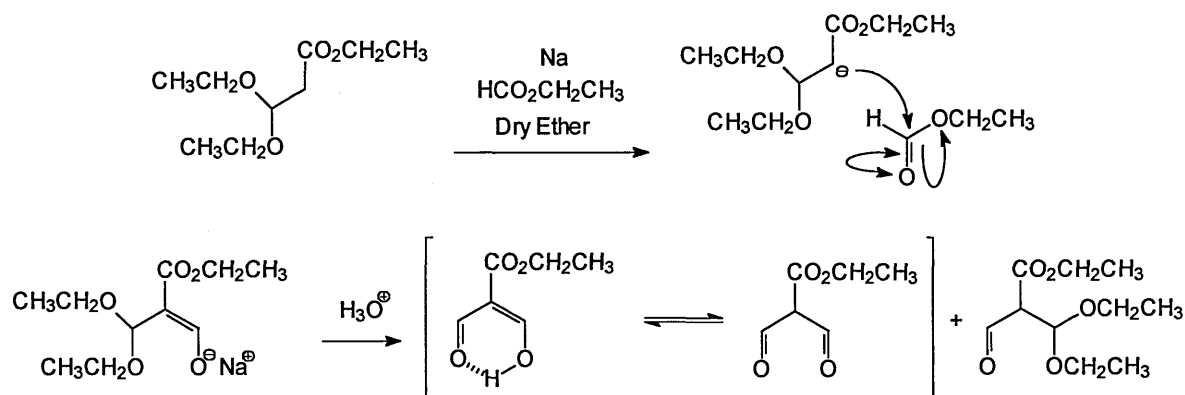


Fig. 2.4 Pannizi reaction for the preparation of 2-carboethoxymalondialdehyde.

The NMR data obtained showed the reaction mixture to contain both the acetal and the 2-carboethoxymalondialdehyde (as well as the presence of some thermal elimination product from the first stage).

The preparation of 2-carboethoxymalondialdehyde became simpler as the precursor, ethyl 3,3-diethoxypropionate became commercially available from several suppliers.

Previous research carried out by this research group identified an alternative method for the preparation of 2-carboethoxymalondialdehyde, which involved the preparation of ethyl formylacetate coupled with a subsequent Pannizi reaction to yield the product. Ethyl formylacetate was prepared via a literature procedure³⁰⁷ from the reaction of a Meldrums acid derivative³⁰⁸ with ethanol in benzene. The dialdehyde was obtained by a Pannizi reaction on the product formyl ester (Fig. 2.5).

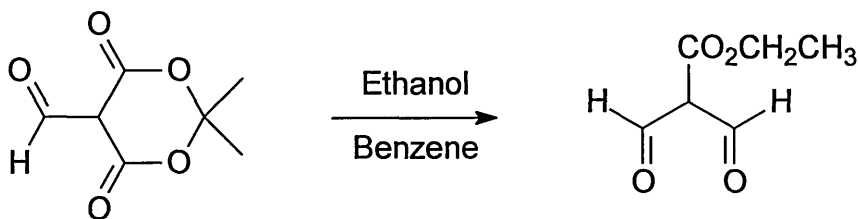


Fig. 2.5 Preparation of 2-carboethoxymalondialdehyde from a Meldrums acid derivative.

The product yields were consistently poor (maximum 35%) and the procedure time consuming since the formyl Meldrums acid was prepared by a three stage synthesis prior to the Pannizi formulation to the ester.

2.2 Preparation of 2-cyanomalondialdehyde (3).

The preparation of 2-cyanomalondialdehyde initially provided problems since there was no simple literature procedure for its formation. The potential use of 2-cyano-3-dimethylaminoacrolein³⁰⁹ (Fig. 2.6) had previously been investigated by the group but the yield of product was extremely low and procedure very lengthy. Attempts to form a mono-Schiff base from the illustrated acrolein were unsuccessful, leading only to a viscous oil of many components.

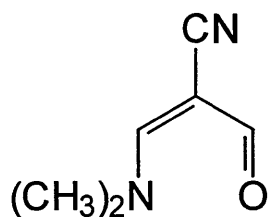


Fig. 2.6 2-cyano-3-dimethyl aminoacrolein

Other proposed routes to obtain 2-cyanomalondialdehyde involve the initial isolation of oxopropanenitrile or its acetal in a Pannizi reaction³¹⁰ to give the dialdehyde. The generation of 3-oxopropanenitrile³¹¹ required, was achieved by the base promoted ring opening of isoxazole, but endeavours to isolate this compound were unsuccessful (no $C\equiv N$ stretching was observed in the IR

spectrum). A one pot ring-opening reaction in the presence of ethyl formate (Fig. 2.7) was also attempted, but again no discernible $C\equiv N$ stretching was observed.

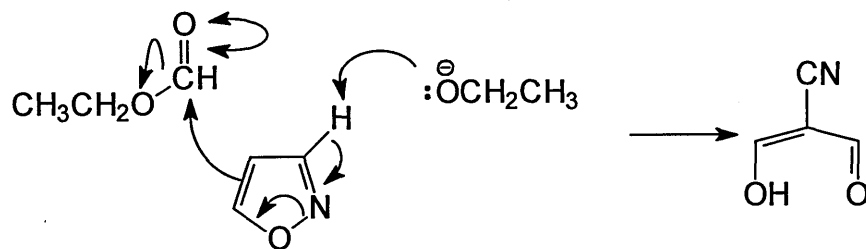


Fig. 2.7 Attempted in-situ use of 3-oxopropanenitrile for the preparation of 2-cyanomalondialdehyde.

A simpler method appeared to be the oxidation of 3-hydroxypropionitrile to the aldehyde with pyridinium dichromate in dichloromethane³¹². The reaction mixture was monitored by solution spectroscopy to observe the appearance of the carbonyl group and the coinciding disappearance of the alcohol group. Comparison spectra after 1 and 21 hours showed little change in the intensity of the alcohol peak, although carbonyl stretching frequencies were present. An ensuing reaction with ortho-phenylenediamine in refluxing ethanol provided no products suggesting that no aldehyde had formed.

The problem of preparing 2-cyanomalondialdehyde was solved when 3,3-diethoxypropionitrile became commercially available. This underwent the Pannizi procedure used for 2-carboethoxymalondialdehyde to yield the desired product (Fig. 2.8).

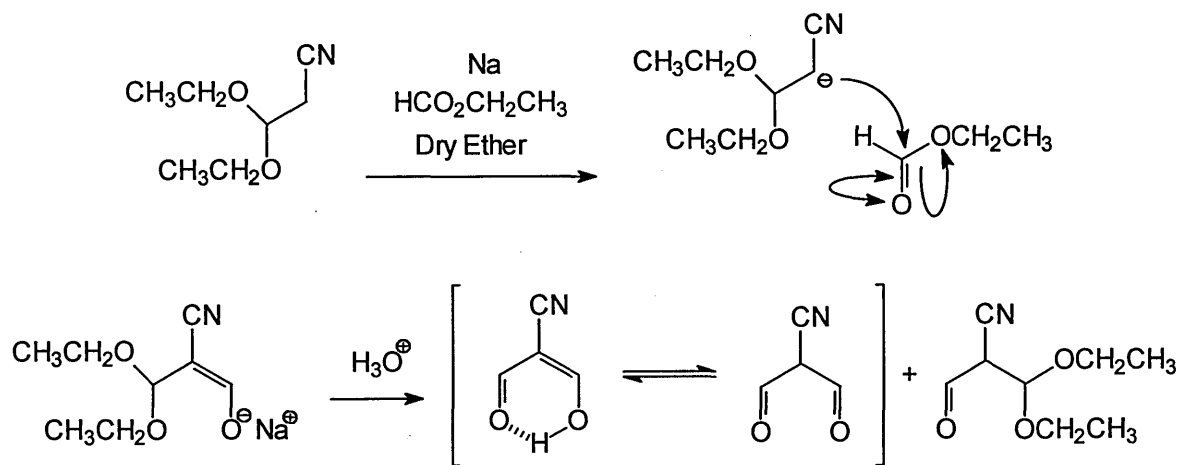


Fig. 2.8 Preparation of 2-cyanomalondialdehyde via the Pannizi reaction.

2.3 Preparation of triformylmethane (5).

The synthesis of triformylmethane may be achieved in several ways that differ not only in technique but also in respect of the salt that is isolated as the intermediate to triformylmethane itself. Prior to 1990 the synthesis of triformylmethane had been achieved by the formylation of 3-dimethylamino-2-propenal³¹³, a malondialdehyde derivative. This starting material can advantageously be replaced by the commercially available 3-diethylamino-2-propenal³¹⁴.

The method of choice for the preparation of triformylmethane involved the use of a simple and efficient two-step procedure²⁷⁷ from bromoacetic acid, phosphoryl chloride and dimethylformamide with the intermediate isolation of a perbromide salt.

The reaction scheme for the two steps is illustrated below (Fig. 2.9).

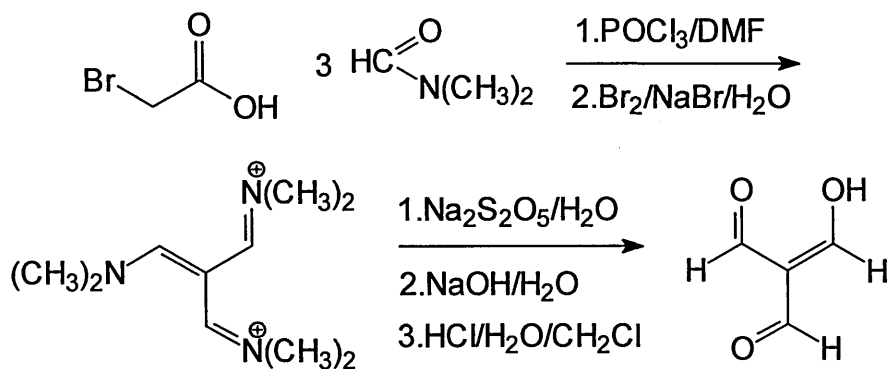


Fig. 2.9 Reaction scheme for the preparation of trimethylmethane.

The mechanism for the preparation of the perbromide intermediate is complicated and involves the reaction of bromoacetic acid with the reagent formed by the reaction of dimethylformamide and phosphoryl chloride. This is an example of the so-called Vilsmeier-Haak synthesis of aldehydes³¹⁵ and the mechanism is illustrated below (Fig. 2.10).

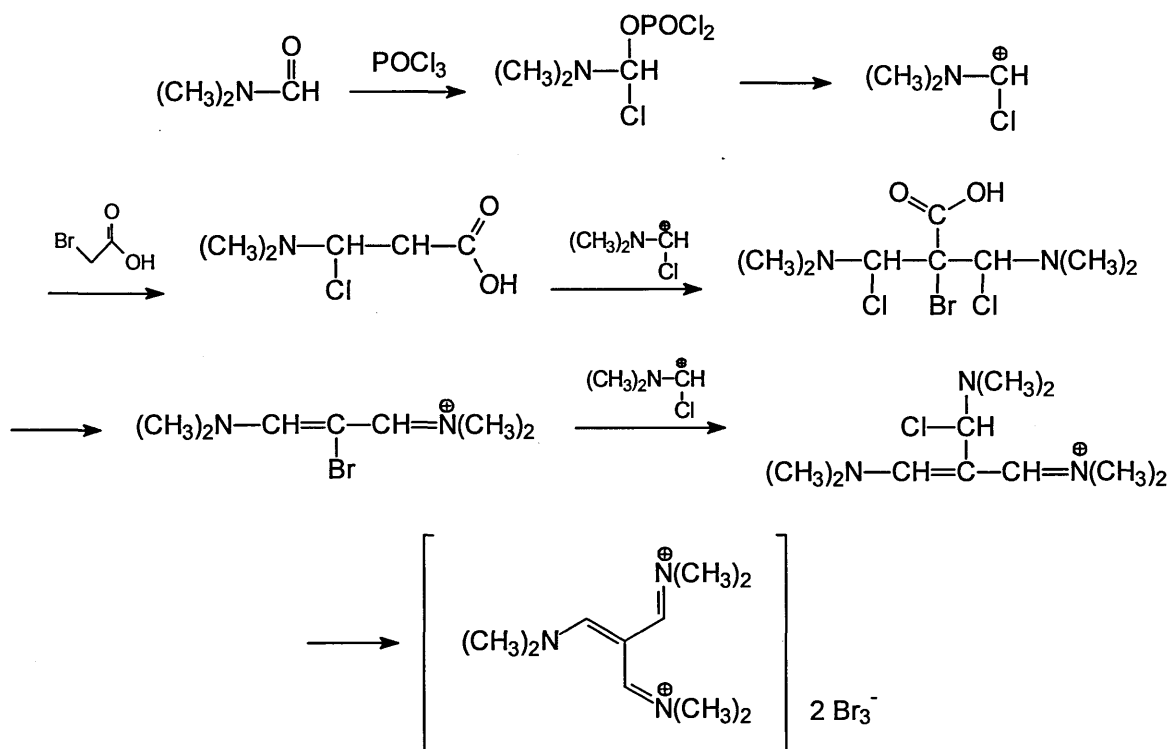


Fig. 2.10 Mechanism for the bis-perbromide intermediate.

2.4 Preparation of sodium 2-nitromalondialdehyde monohydrate (7).

Sodium 2-nitromalondialdehyde monohydrate³⁰² was prepared by the reaction of mucobromic acid (6) with aqueous sodium nitrite to yield the product as salmon pink needles. Caution was taken during the procedure as hydrogen cyanide was liberated (1g/kg of mucobromic acid used), and care was also essential for the subsequent storage and handling of sodium 2-nitromalondialdehyde monohydrate as the material is impact sensitive and thermally unstable. The material should therefore be treated as a potential explosive.

Mucobromic acid³⁰² was prepared by the reaction of distilled furfural, water and bromine at a temperature of below 5°C. The reaction was driven to completion by reflux and the excess bromine removed by distillation of the solution until the distillate was almost colourless (the hydrobromic acid was condensed using a nitrogen trap). Evaporation of the solution afforded the crude mucobromic acid which was recrystallised from boiling water to enable the isolation of colourless crystals. The reaction scheme for the preparation is illustrated below (Fig. 2.11).

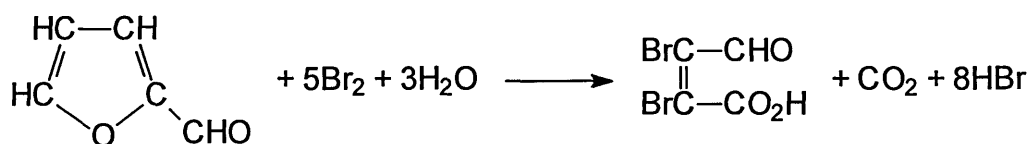


Fig. 2.11 Reaction for the preparation of mucobromic acid.

Sodium 2-nitromalondialdehyde was prepared by the reaction of the mucobromic acid with aqueous sodium nitrite. A solution of mucobromic acid in 95% ethanol was added dropwise to the sodium nitrite at a temperature of 52-56°C resulting in a colour change to deep red and an exothermic reaction. The evolution of a gas was also observed. The product was carefully collected on a previously chilled Büchner as a moist cake, which was recrystallised from 75% ethanol to yield the product as salmon pink needles (Fig. 2.12).

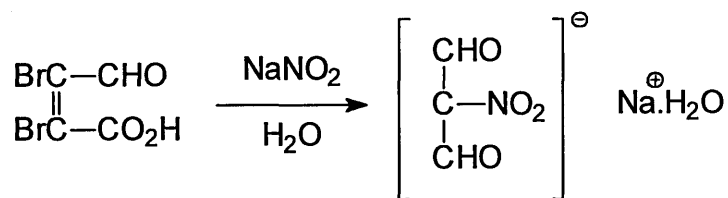


Fig. 2.12 Reaction for the preparation of sodium 2-nitromalondialdehyde monohydrate.

2.5 Preparation of 2-bromomalondialdehyde(8).

The preparation of 2-bromomalondialdehyde²⁹³ was carried out by the bromination of malonaldehyde bis-(diethyl acetal) in concentrated hydrochloric acid. The reaction yield was found to be dependent on the rate of addition of bromine to the vigorously stirred solution of the bis-acetal. Consequently the rate of addition was controlled such that the temperature of the reaction solution did not rise. The reaction equation is illustrated below (Fig. 2.13).

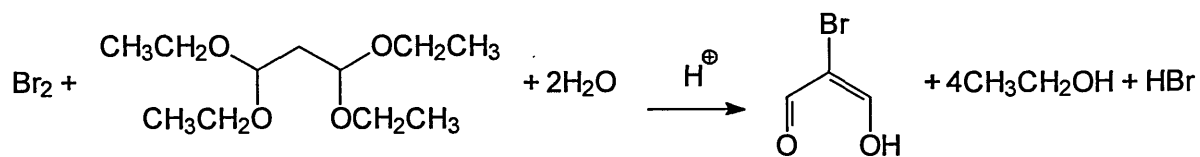


Fig. 2.13 Preparation of 2-bromomalondialdehyde.

2.6 The preparation of 2-Carboethoxymalondialdehyde bis(diethylacetal) (9)

It can clearly be seen that the protection of malondialdehydes as their acetals opens up the possibility of further derivatives if the initial malondialdehyde contains a reactive substituent at the 2-position of the molecule. Consequently, attempts were made to manufacture the bis-acetal of 2-carboethoxymalondialdehyde (Fig. 2.14) in the hope that the reactivity of the ester would enable the formation of further derivatives.

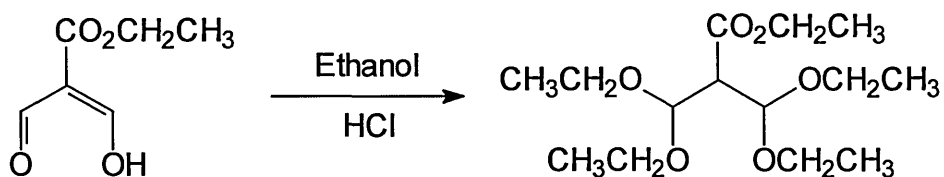


Fig. 2.14 Preparation of 2-Carboethoxymalondialdehyde bis(diethylacetal)

The preparation of acetals is well documented³¹⁶ and essentially involve the reaction of an aldehyde or ketone with an alcohol in the presence of an acid or base catalyst. The mechanism for the acid catalysis preparation of an acetal is illustrated below (Fig. 2.15). Protonation of the carbonyl promotes the nucleophilic attack by the oxygen atom of the alcohol thus producing the hemiacetal. Protonation of the tertiary alcohol and the subsequent loss of water leads to the resonance stabilised carbocation, which may undergo nucleophilic attack by a second alcohol molecule to yield the acetal.

Acetals are extremely useful as protecting agents as they are stable to aqueous bases, organometallics and hydride reducing agents but are unstable to dilute aqueous acid.

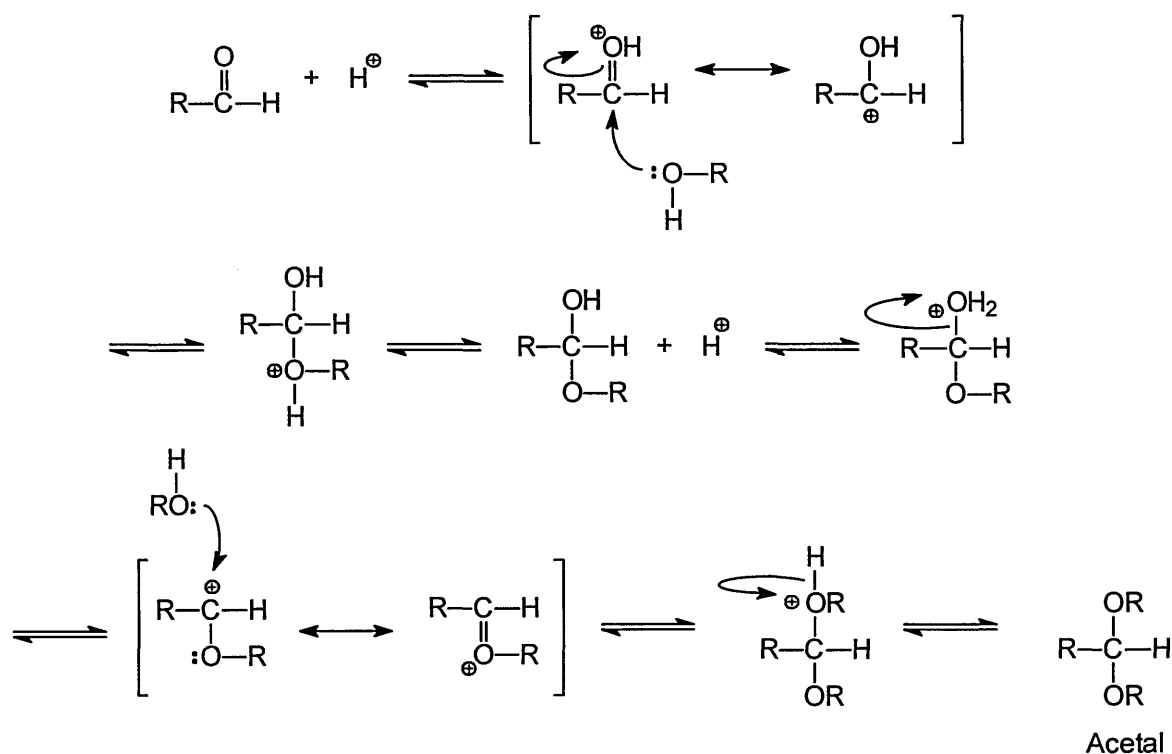


Fig. 2.15 Mechanism for acetal formation.

The protection of the aldehyde functionalities as their acetals was attempted in several ways with differing success. The experimental section of this thesis has already documented five procedures that were used in the attempt to prepare the bis-acetal (Chapter 5 - section 3.9). The procedures essentially involved the dropwise addition of 2-carboethoxymalondialdehyde to a stirred solution of ethanolic hydrochloric acid, or the bubbling of dry HCl gas to a stirred solution of 2-carboethoxymalondialdehyde in dry ethanol. In the first method the isolation of the acetal was not attempted and consequently the product is a solution of the bis-acetal in ethanolic HCl. Spectroscopic data was not obtained as it was not the pure material. The isolation of the acetal was attempted during methods 2 and 3. Both of these methods had essentially the same work-up, however, the initial reaction was slightly different since the acetal formation of method 2 was attempted by simply stirring the reagents under nitrogen overnight whilst that of method 3 was achieved by refluxing the reagents for two hours under nitrogen. The work up of the solutions then followed the same line. Firstly excess HCl was neutralised by the addition of a suspension of solid sodium carbonate in saturated sodium bicarbonate resulting in a colour change from red to yellow. The purification of the material was achieved by solvent extraction with water and dichloromethane which afforded the bis-acetal in the organic layer. The amber liquid afforded by the stirring procedure provided a mass spectra data that was complex but did exhibit an ion with a m/z ratio equivalent to that of one of the acetal groups i.e. $[(\text{CH}_3\text{CH}_2)_2\text{OCH}]^+$. Examination of the solution by TLC revealed that a reaction had occurred but the classification of a product spot could not be made. The plate revealed that the product solution contained both the starting material and the acetal since both positive and negative responses to dinitrophenylhydrazine were observed. The material produced by the refluxing also had a peak corresponding to $[(\text{CH}_3\text{CH}_2)_2\text{OCH}]^+$ in the mass spectrum. TLC with dichloromethane as the solvent showed the presence of two spots with increased R_f values compared with the 2-carboethoxymalondialdehyde, indicating that both the mono- and bis-acetals had been formed. However, it was later established that both spots gave a negative response for aldehydes when sprayed with dinitrophenylhydrazine thus discounting the presence of a mono-acetal. The TLC also illustrated the presence of a small amount of unreacted starting material which was confirmed by the presence of an O-H stretch peak in the IR spectrum.

Method 3 in section 3.9 of chapter 4 details a procedure where the acetal formation is by the basic addition of 2-carboethoxymalondialdehyde to a stirred ethanolic HCl solution, but the removal of the ethanolic HCl liquor was attempted by rotary evaporation. The beige solid which was isolated was found to contain HCl due to the characteristic splitting pattern of chlorine for the ions at m/z ratios of 36 and 38 in the mass spectrum. This explains the hygroscopic nature of the material as the concentrated acid acts as a desiccant.

Acetalisation of 2-carboethoxymalondialdehyde was also attempted by the Arnold procedure²⁷⁷ utilising the reaction of the aldehyde functionality with triethylorthoformate in the presence of a perchloric acid catalyst. Neutralisation of the acid with a methanolic NaOH solution allowed removal of the volatiles under reduced pressure. The material was purified by vacuum distillation. Mass spectral examination of the colourless liquid again showed the presence of an ion corresponding to $[(\text{CH}_3\text{CH}_2)_2\text{OCH}]^+$ at a m/z ratio of 103. The ^1H NMR confirmed the structure of the material although the multiplicity of methine carbons that had been the carbonyl functionalities was found to be a singlet where a doublet may have been expected. The difference between the chemical shifts that initially may be expected to be identical due to their similar environment, may explained by the formation of a double bond in the equilibrium system illustrated below (Fig. 2.16). The double bond stops the free rotation of the unsymmetrical ester portion of the molecule allowing hydrogen bonding between the alcohol and the oxygen atom of the ether group. The shielding of the H_A atom is increased and consequently the peak is shifted upfield.

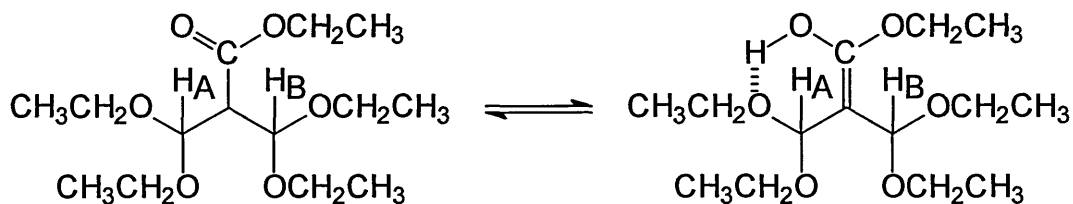


Fig. 2.16 Equilibrium of 2-malondialdehyde bis(diethylacetal).

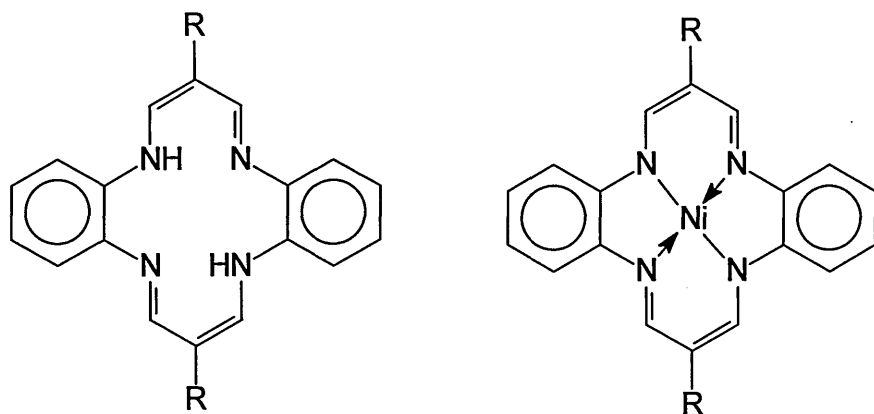
2.7 The preparation of 2-Hydroxymethylenemalondialdehyde bis(diethyl acetal) (10)

2-Carboethoxymalondialdehyde bis(diethyl acetal) (9) (3.9 method 1) was reduced by reaction of the acetal with LiAlH_4 in cold (ice bath), dry ether. The red/black liquid isolated afforded spectral data that confirmed the reduction of the ester to an alcohol due to the appearance of an O-H str. peak in the infra-red spectrum. All chemical shifts and peak multiplicities in the ^1H NMR spectrum correlated with the theoretical values. Although the hydroxyl proton at a chemical shift of 0 - 4.5 was noticeably absent. The peak may have been masked by other peaks in the spectrum. Mass spectral data was complex although an ion corresponding to $[(\text{CH}_3\text{CH}_2)_2\text{OCH}]^+$ was present in the spectrum. It should be noted that after the experiment had been performed discussion within the research group established the dangers associated with this procedure. LiAlH_4 is reckoned to ignite ethanol and explode with HCl, consequently it is not recommended that the procedure is repeated.

The LiAlH_4 reduction of acetals previously described (3.9 methods 4 & 5) was found to be unsuccessful.

3. Macrocycles and macrocyclic complexes based upon dibenzotetraaza[14]annulenes.

The template and non-template preparation of substituted macrocycles, to produce both the free ligands and metal complexes, have been developed from established literature procedures as well as novel methods. The development and use of malondialdehydes has allowed extensions to be made to the series based upon the dibenzotetraaza[14]annulene ring system (Fig. 3.1).



1. R = Br

2. R = CO₂CH₂CH₃

3. R = NO₂

4. R = CHO

5. R = CN

6. R = NO₂

7. R = CO₂CH₂CH₃

8. R = H

Fig. 3.1 Macrocyclic free ligands and complexes prepared.

3.1 Free ligand macrocycles.

The preparation of free ligand macrocycles was achieved in all cases by the Schiff base condensation of a substituted malondialdehyde with ortho-phenylenediamine (or a derivative). Purification of the materials utilising conventional recrystallisation techniques was unsuccessful. Soxhlet extraction of the materials was found to be of some use, but by far the best method was found to be a sacrificial recrystallisation using chloroform and methanol. The sacrificial method enabled the purification of only two of the above free ligand macrocycles, namely the nitro and carboethoxy derivatives.

3.1.1 6,13-Dicarboethoxy-dihydrodibenzo[b,i][1,4,8,11]tetraazacyclotetradecine

The di-carboethoxy substituted macrocycle was isolated as a bright orange solid that was purified by sacrificial recrystallisation. The peaks observed in the solid state ^{13}C NMR spectra of the material (Fig. 3.2) were found to correlate to those expected by theory. A peak corresponding to the para-aryl carbon is absent since that due to the dual amino substitution means the carbon located para to one amine functionality is located meta to the second amine functionality, and vice versa.

^{13}C NMR spectra	δ 13.8	CH_2CH_3
	δ 60.9	CH_2CH_3
	δ 100.8	Ph-N=C-
	δ 114.8	Ortho aryl C
	δ 125.1	Meta aryl carbon
	δ 135.9	$\text{C-CO}_2\text{CH}_2\text{CH}_3$
	δ 144 - 154	Ph-NH
	δ 166.1	-CO-O-
Infra-red spectra	3450cm^{-1}	N-H str. - 2° amine
	3080cm^{-1}	C-H str. - aryl
	2990cm^{-1}	C-H str. - aliphatic
	1700cm^{-1}	C=O str. - esters
	1630cm^{-1}	C=C str. - aryl
	1580cm^{-1}	N-H bend - 2° amine
	1450cm^{-1}	C-H bend - aliphatic
	1255 and 1315cm^{-1}	C-O str. -esters

3.1.2 6,13-Dinitro-dihydrodibenzo[b,i][1,4,8,11]tetraazacyclotetradecine

The di-nitro substituted macrocycle was isolated as a red solid that was purified by sacrificial recrystallisation. The peaks observed in the solid state ^{13}C NMR spectra of the material (Fig. 3.3) were found to correlate to those expected by theory. However, due to the broad range given for the chemical shift of particular functionalities in NMR data tables the attribution of the peaks could not be made in all cases. A peak corresponding to the para-aryl carbon is absent for the same reason as previously cited for the di-carboethoxy macrocycle. Essentially that due to the dual amino substitution means the carbon located para to one amine functionality is located meta to the second amine functionality, and vice versa. One anomaly noticed in the spectrum was the presence of six peaks when we might only expect four. This may be due to equilibrium structures of the macrocycle.

^{13}C NMR spectra	δ 146	<u>Ph</u> -N or - <u>C</u> H=N
	δ 135	<u>Ph</u> -N
	δ 128	Meta aryl C
	δ 126.5	Meta aryl C
	δ 118	
	δ 115	Para aryl C
Infra-red spectra	3440cm^{-1}	N-H str. - 2° amine
	3050cm^{-1}	C-H str. - aryl
	2990cm^{-1}	C-H str. - aliphatic
	1580 and 1500cm^{-1}	C=Cstr. - aryl
	1555 and 1350cm^{-1}	N=Ostr. - nitro
	1380 and 1430cm^{-1}	C-H bend - aliphatic
	645cm^{-1}	N=O bend - nitro

3.2 Symmetrical macrocyclic complexes.

The preparation of the three macrocyclic complexes illustrated previously (Fig. 3.1) was undertaken by two methods. The preparation of compounds 6 and 7 utilised the procedure adopted for the free ligands. That is to say equimolar quantities of the appropriate malondialdehyde and ortho-phenylenediamine along with nickel(II) acetate were stirred in a suitable solvent in the dark. The solid isolate was purified by a sacrificial recrystallisation to yield the macrocyclic complex.

The preparation of macrocyclic complexes via the utilisation of uncyclised metal chelates²⁹⁵ allowed the preparation of macrocycle 8 and has been extended to prepare novel 1-D unsymmetrical macrocyclic complexes which will be discussed later.

The uncyclised metal chelate of choice, [N,N''-(1,3-propanediylidene) bis(1,2-benzenediaminato)-N,N',N'',N''']nickel(II) hexafluorophosphate, is illustrated below (Fig. 3.2).

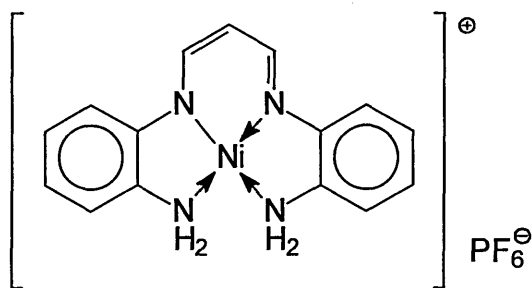


Fig. 3.2 Uncyclised metal chelate.

Preparation of the $\frac{3}{4}$ macrocyclic complex was achieved by the procedure described by Dolphin, Alleyne and Cutler²⁹⁵ involving the one stage reaction of ortho-phenylenediamine, nickel(II) chloride and malonaldehyde bis(diethyl acetal) in the presence of ammonium hexafluorophosphate. Ring closure of the complex by reflux under nitrogen with malondialdehyde bis(diethyl) acetal in a 90% aqueous solution of dimethylformamide afforded the symmetrical macrocycle

dihydrodibenzo[b,i][1,4,8,11]tetraazacyclotetradecine nickel(II), which is the parent macrocycle of the Hiller type (Fig. 3.3).

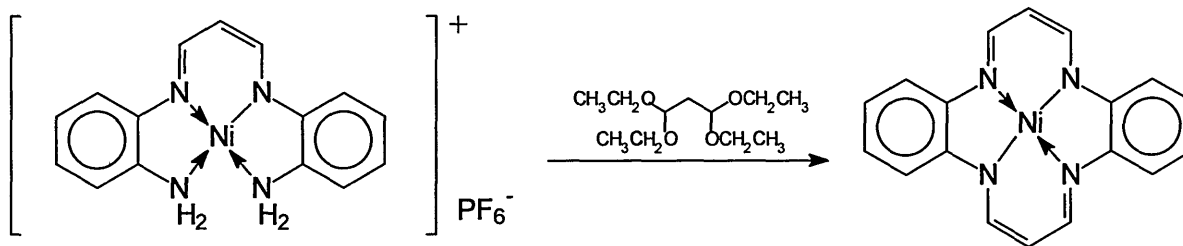


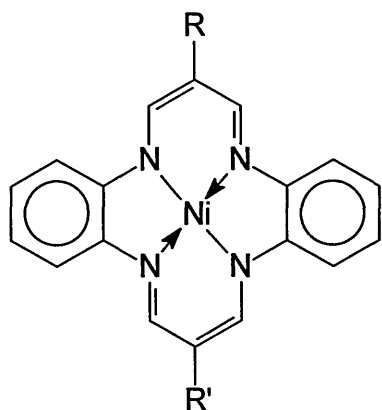
Fig. 3.3 Preparation of macrocyclic metal complexes from uncyclised metal chelate.

3.3 Unsymmetrical macrocyclic complexes.

The preparation of unsymmetrical macrocyclic complexes is of major interest in current research in respect of the semiconducting and liquid crystalline characteristics that may be exhibited by this type of molecule, as well as their relationship to the bio-organic compounds to which they are related. The synthetic strategy adopted has involved two techniques. The first involves the use of uncyclised metal chelates which may be reacted with substituted malondialdehydes, and the second utilises various protecting strategies throughout the synthesis to create macrocyclic complexes that are unsymmetrical in two dimensions.

3.3.1 Unsymmetrical macrocyclic complexes from uncyclised metal chelates.

The utilisation of the technique described in section 3.2 for the preparation of the parent Hiller macrocycle may also be used for the preparation of unsymmetrical macrocycles. Essentially the uncyclised metal chelate (Fig. 3.3) was reacted with the substituted malondialdehyde of choice by reflux in 90% aqueous dimethylformamide under nitrogen to form the 1-D macrocyclic complex. The series of macrocyclic complexes studied is illustrated below (Fig. 3.4).



9. $R = H, R' = CO_2CH_2CH_3$
 10. $R = H, R' = Br$
 $R = H, R' = CHO$
 $R = H, R' = CN$

Fig. 3.4 1-D unsymmetrical macrocyclic complexes.

The mass spectra of the complexes all exhibited the expected molecular ion peak. However, although this technique was found to be a successful procedure for the preparation of the 1-D macrocyclic complexes illustrated above the microanalysis of the materials did not conform to the expected C, H and N ratios. Time constraints did not allow for the investigation into a method for the purification of the complexes although it might be expected that the sacrificial recrystallisation used successfully in previous examples may have been employed in this case.

3.3.2 Synthesis of 2-D unsymmetrical macrocyclic complexes.

The requirement for the development of macrocycles that are unsymmetrical in nature has previously been discussed (chapter 4). Essentially the preparation of such materials has arisen due to the limitations in terms of solubility and molecular interactions associated with symmetrical macrocycles. The creation of an unsymmetrical molecule (Fig. 3.5) may lead to the development of a compound with enhanced solubility, electrical conduction and liquid crystalline characteristics.

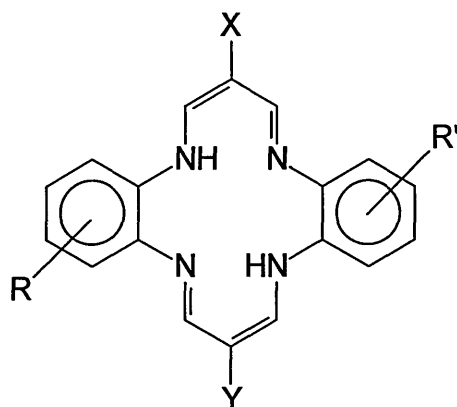


Fig. 3.5 Unsymmetrical Dibenzotetraaza[14]annulene.

These enhanced characteristics are a result of the dipole that is induced by the unsymmetrical nature of the molecule. This promotes an ordered configuration by the alignment of the dipoles, and as a result an enhancement of characteristics that are promoted by this feature, such as liquid crystallinity and electrical conduction may be achieved.

The preparation of 2-D unsymmetrical macrocyclic complexes based upon the dibenzotetraaza[14]annulene ring system has, as might be expected, been approached by the condensation of two equivalents of different diamine with two equivalents of different dicarbonyl. Direct attempts at this approach resulted in product mixtures that defied attempts to isolate useful amounts of the unsymmetrical product. The approach to the problem has been the use of protecting groups and has allowed the synthesis of the nickel(II) complex of the macrocycle illustrated (Fig. 3.6).

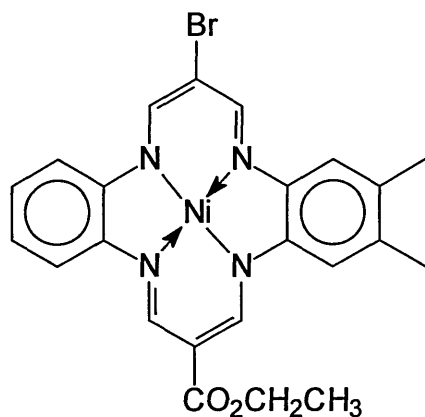


Fig. 3.6 2-D unsymmetrical macrocyclic complex.

3.3.2.1 Synthetic approaches for the formation of unsymmetrical macrocycles.

Many approaches to the formation of unsymmetrical macrocycles may be envisaged and in order to understand the reasoning behind the eventual solution to the problem the information from available literature and the research previously undertaken within the group must be discussed.

Previous Work

a. Diamino Compounds

The preparation of unsymmetrical dibenzotetraaza[14]annulenes via the Schiff base condensation of aldehydes with amines has one major problem, namely that an efficient synthetic approach is not possible due to the many possible side reactions that may occur. These may result in the formation of molecules such as imidazoles, benzodiazepines and polymeric material (Fig. 3.7)

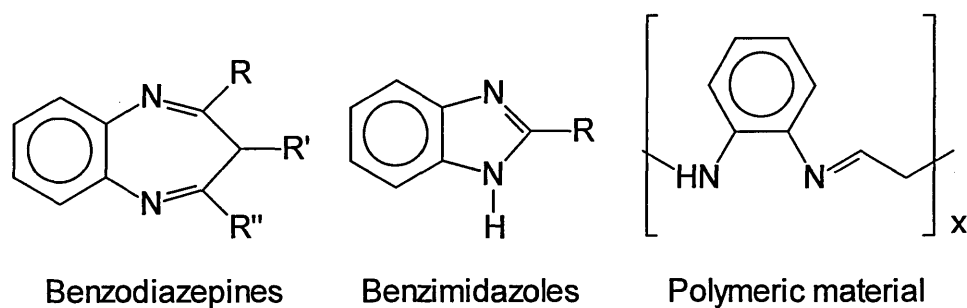


Fig. 3.7 Side products of Schiff bases condensations.

The utilisation of protected diamines (notably ortho-nitroaniline derivatives) offer a certain degree of control in the synthetic approach to the formation of unsymmetrical macrocycles (Fig. 3.8).

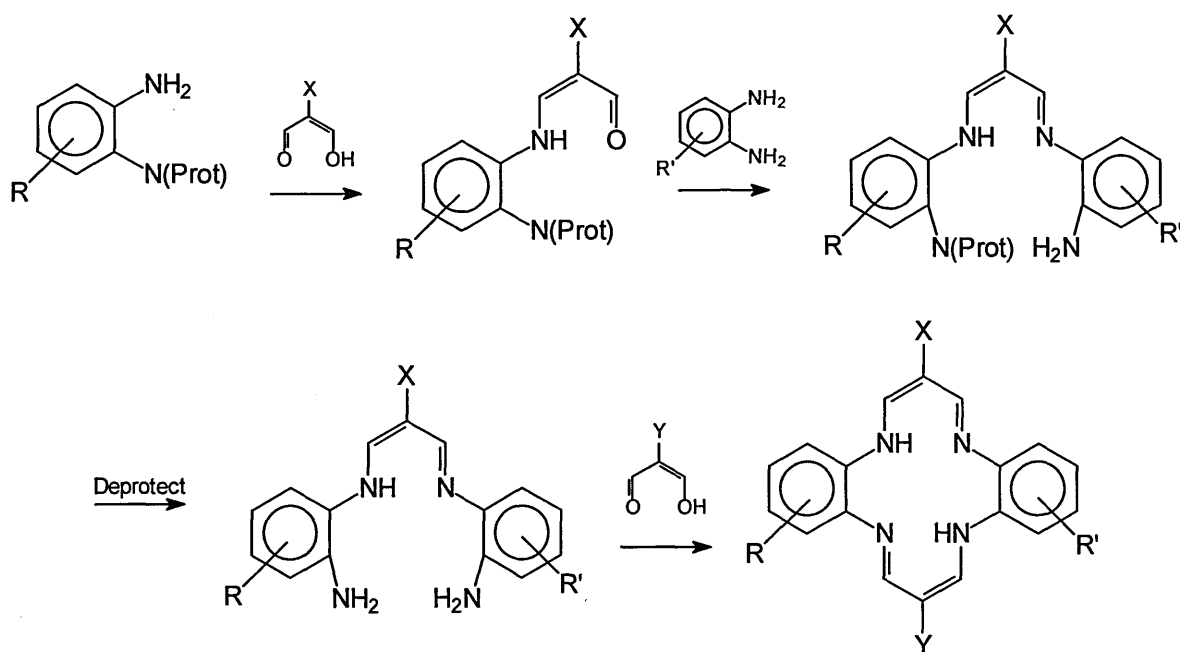


Fig. 3.8 Use of protected amines for the preparation of unsymmetrical DBTAA's

Ortho-nitroanilines may be viewed as masked diamines since the nitro group may be readily reduced to the amine³¹⁷. However, the conditions employed must be mild since the Schiff base contains the readily reduced C=N linkage. Additionally the stage at which reduction is instigated is important; for example reduction of the nitro group during the deprotection stage illustrated above may lead to the formation of benzodiazepines^{318,319} by a rapid ring closure step that follows the reduction. The protection and deprotection of primary amine groups is most commonly used in peptide synthesis where ease of introduction, stability under the reaction conditions employed and subsequent selective removal are all key factors for successful results. As such the properties of available protecting groups are well researched and a wide range of strategies are available. A few examples of such protecting groups are the benzyloxycarbonyl³²⁰, t-butoxycarbonyl³²¹, fluorenylmethoxycarbonyl³²² and phthaloyl derivatives³²³.

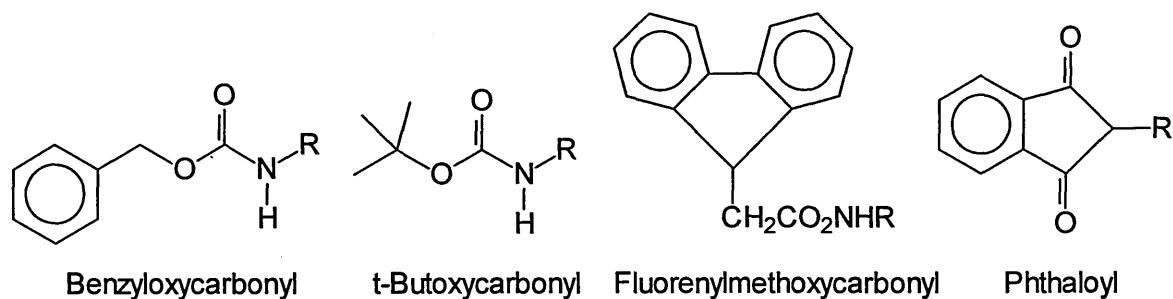


Fig. 3.9 Protecting groups.

Modification of reaction conditions and solvents may be required to accommodate the aromatic amines utilised during the course of research. Another important consideration is that deprotection reactions must not effect other labile groups present in the molecule, such as imine linkages

b. β -Dicarbonyl compounds

It has previously been shown (chapter 4) that the preparation of macrocyclic molecules may be achieved by the condensation of aromatic diamines with β -dicarbonyl compounds. As a result of this, research was undertaken by the group³²⁴ into the efficient preparation of both known and novel dicarbonyls, in particular β -dialdehydes. Unlike the aromatic diamine components of proposed macrocycles few malondialdehyde derivatives are available commercially and therefore the majority have been synthesised.

The reactive nature of malondialdehydes often requires them to be stored as the acetal. It may be imagined that the protection of malondialdehydes as their acetals allows entry into the preparation of other malondialdehydes by modification of the substituent at the 2-position. The use of a variety of 2-substituted malondialdehydes may allow the development of a series of malondialdehydes with differing electronic properties due to the variation of characteristics such as polarity within the malondialdehydes. Other properties such as solubility may also be dependent on the nature of the substituent.

The development of a method for macrocycle formation may also be approached by the use of protected carbonyl functionalities (Fig. 3.10)

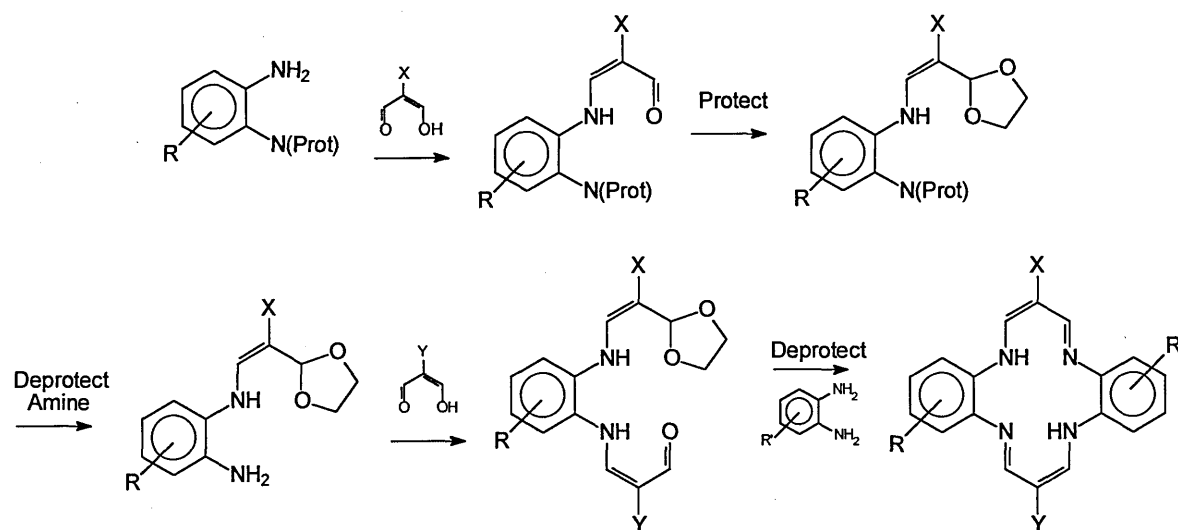


Fig. 3.10 Protection of carbonyl functionalities for the preparation of DBTAA's

Mono-acetalised diamines may undergo reactions that allow a selective synthesis onto one aldehyde group. However, only a few of general applicability have been reported in the literature³²⁵, and these generally deal with the malondialdehyde itself, not the 2-substituted derivatives which may give mixtures of products. A method for the preparation of halo-malonaldehyde mono-acetals has been noted although the procedure is complicated and has not as yet been evaluated.

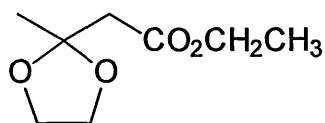


Fig. 3.11 Acetal of ethylacetoacetate

The acetal of ethyl acetoacetate (Fig. 3.11) has been prepared using a Dean-Stark apparatus. The Claisen type condensation³²⁶ to yield the 2-carboethoxymalondialdehyde was attempted with several bases (sodium ethoxide, sodium hydride and lithium di-isopropylamide) but the required product was not obtained. It was thought that the reason behind this may be steric problems associated with the methyl group.

c. Protection of the amino group

In order to understand the reasoning for our synthetic strategy toward 2-D unsymmetrical macrocycles it is necessary to examine the previous research undertaken by the group. Much of this work has until now been unpublished.

It was thought that the most promising route for the preparation of 2-D unsymmetrical dibenzotetraaza[14]annulenes was that utilising the protection of the amine groups of ortho-phenylenediamine in a stepwise synthesis.

Ortho-phenylenediamine reacted with an equimolar quantity of N-carboethoxyphthalimide in ethanol to yield the mono-protected diamine (Fig. 3.12) in yield of up to 90%. Removal of the phthalimido group was facilitated by heating the product in methanol with hydrazine monohydrate (1:1 mixture). This resulted in the isolation of a product mixture of the original amine and the expected phthalhydrazide.

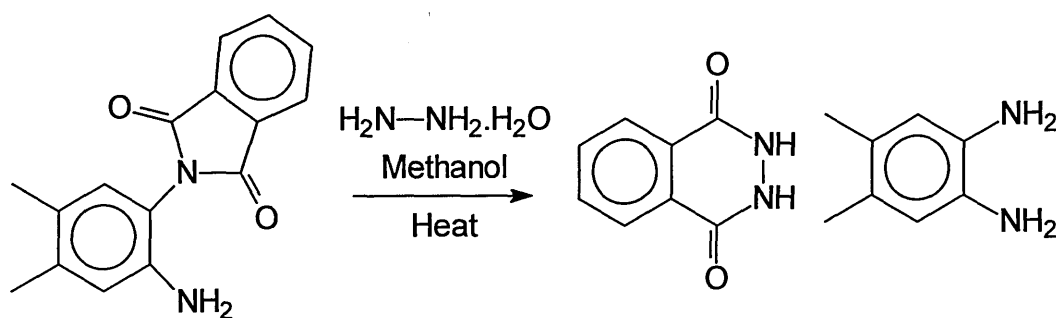


Fig. 3.12 Phthalimido deprotection

The mono-protected amine illustrated above resulted in the corresponding Schiff base when reacted with 2-carboethoxymalondialdehyde (Fig. 3.13). The attempted deprotection by removal of the phthaloyl group resulted in the loss of the imine with the compound illustrated as the starting material in fig. 3.12 being isolated as the solid product. This may be explained by the transamination reaction

(discussed later) in which the addition of hydrazine to the imine group occurs in preference to the intended nucleophilic attack at the carbonyl centres.

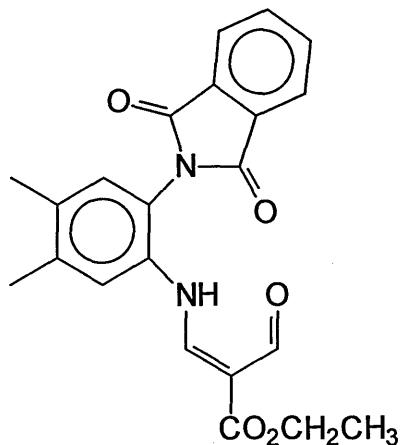


Fig. 3.13

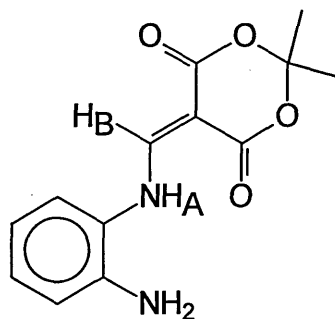


Fig. 3.14 Meldrums acid derivative

Ortho-phenylenediamine was found to condense, in refluxing ethanol, with an equimolar amount of formyl meldrums acid³²⁷ to give the compound illustrated (Fig. 3.14). The infra-red spectrum was found to contain peaks at 3350 and 3200cm⁻¹ corresponding to N-H str. The ¹H NMR spectrum exhibited the following important peaks:

H _A	11	1H, d
H _B	8.3	1H, d
N-H	3.55	2H, s (broad)

The compound illustrated (Fig. 3.14) was found to form a second Schiff base on reaction with either 2-bromomalondialdehyde or 2-carboethoxymalondialdehyde in tetrahydrofuran. The product of the reaction is illustrated below (Fig. 3.16). Purification of the materials and characterisation by ¹H NMR and IR spectroscopy confirmed their identity. It was considered that if the molecule could adopt the above conformation it may be possible to form a macrocycle as the cyclic ester of Meldrums acid. This could theoretically lose acetone to give an amide linkage (Fig. 3.17)

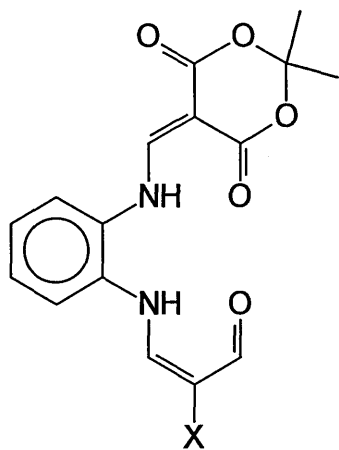


Fig. 3.16 X = Br, CO₂CH₂CH₃

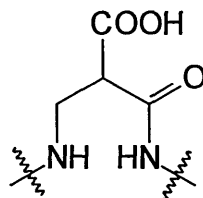


Fig. 3.17

However, no macrocycle was obtained from the reaction, even with the metal ion present to act as the template. In a further attempt to produce a macrocycle the carbonyl function of the Meldrum's acid derivative was reacted with an amine. A transimination reaction was found to occur resulting in the formation of the 4,5-dimethyl substituted derivative (Fig. 3.18).

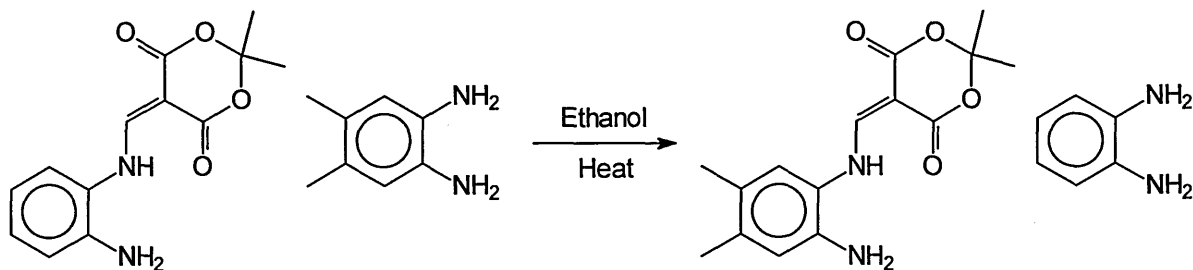


Fig . 3.18 Transimination reaction

It would appear that the 4,5-dimethyl-1,2-phenylenediamine was able to displace the less nucleophilic ortho-phenylenediamine within a relative short reaction time.

3.4 Transimination - Amine Exchange³²⁸

The process whereby the amine component of an imine or Schiff base is exchanged may be called 'transimination' or amine exchange. For our purpose the term 'transimination' is preferred as an analogy to the transesterification process. It should be noted that all stages in the acid catalysed preparation of imines from carbonyl compounds are reversible. Consequently, imines are readily hydrolysed by aqueous mineral acids to the starting components³²⁹. Just as water adds to imines, so should primary and secondary amines. The intermediate 1,1-diaminoalkane (Fig. 3.19) is not stable and in the case of secondary amines no reaction occurs because deamination of the intermediate can only give the starting materials.

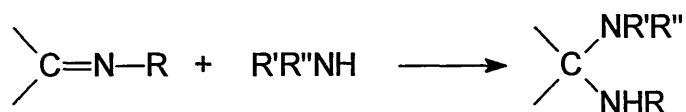


Fig. 3.19

In the case of primary amines the intermediate now has two possible means of deamination and consequently an exchange reaction can occur. A possible mechanism for the acid catalysed transimination reaction is illustrated below (Fig. 3.20).

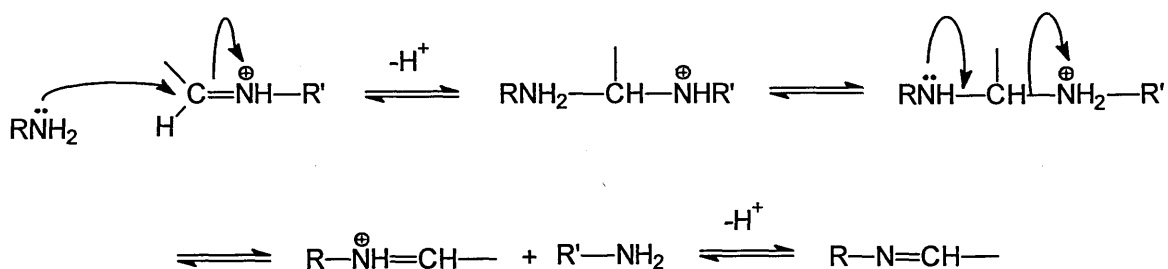


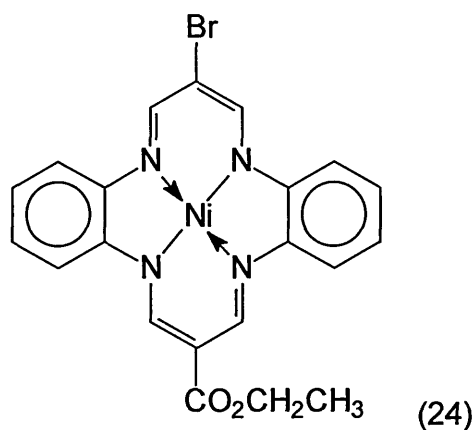
Fig. 3.20

This exchange was first used by Ruddlelien³³⁰ to obtain imines. It was found that amine exchange occurs more readily when the displacing amine has a greater basicity (or a greater nucleophilicity) than the liberated amine³³¹, with the rate of displacement being dependent on the steric constraints

placed upon the incoming and outgoing amines. A few examples of amine exchange reactions at coordinated imine centres have been reported³³²⁻³³⁴.

3.5 The preparation of a 2-D macrocyclic complex of nickel (II) : 6-Carboethoxy-13-bromo-dihydrodibenzo-4,5-dimethylbenzo[b,i][1,4,8,11] tetraazacyclotetradecine nickel (II) (24)

As previously discussed the synthesis of 2-D unsymmetrical macrocyclic complexes requires the implementation of a protecting group strategy to prevent the formation of complex product mixtures that defy all attempts at purification. Using the results gained previously within the group allowed a procedure to be developed for the preparation of 6-Carboethoxy-13-bromo-dihydrodibenzo-4,5-dimethylbenzo[b,i][1,4,8,11] tetraazacyclotetradecine nickel (II) (24) using a six step synthesis.



Ortho-phenylenediamine was selected as a suitable starting material onto which the macrocyclic framework would be sequentially built to yield the macrocycle. The initial requirement was the protection of one of the amine groups of the diamine. Selection of the allyloxycarbonyl derivative, as the protecting agent, produced under Schotten-Baumann conditions proved to be effective and allowed isolation of the mono-protected diamine (25). The reaction was performed in alkaline dichloromethane using the dropwise addition of allyl chloroformate which, following evaporation, trituration and purification by column chromatography (ethyl acetate/petrol/chloroform – 20:30:50) the

mono-protected anil was isolated as a beige powder at a yield of 46% (Fig. 3.21). Purity was confirmed by TLC and the material also confirmed to expected MS, IR and microanalysis.

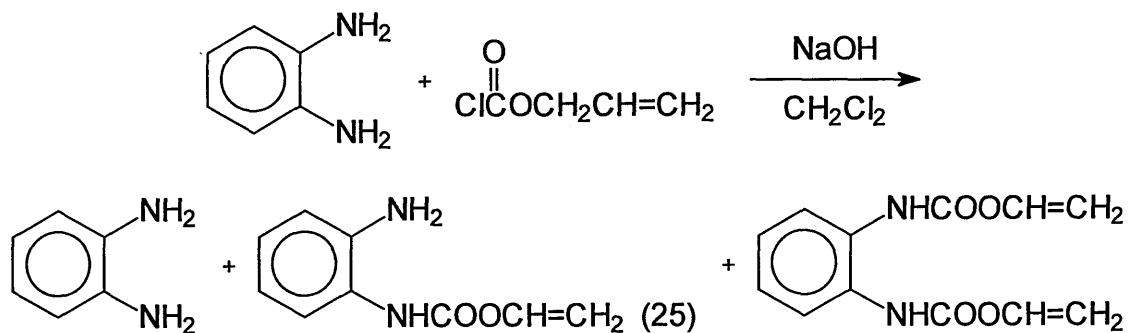


Fig. 3.21

Condensation of 25 with bromomalondialdehyde (8) in refluxing tetrahydrofuran with a para-toluenesulphonic acid catalyst allowed isolation of the mono-protected mono-anil as shown in the remaining synthetic strategy (Fig. 3.22)

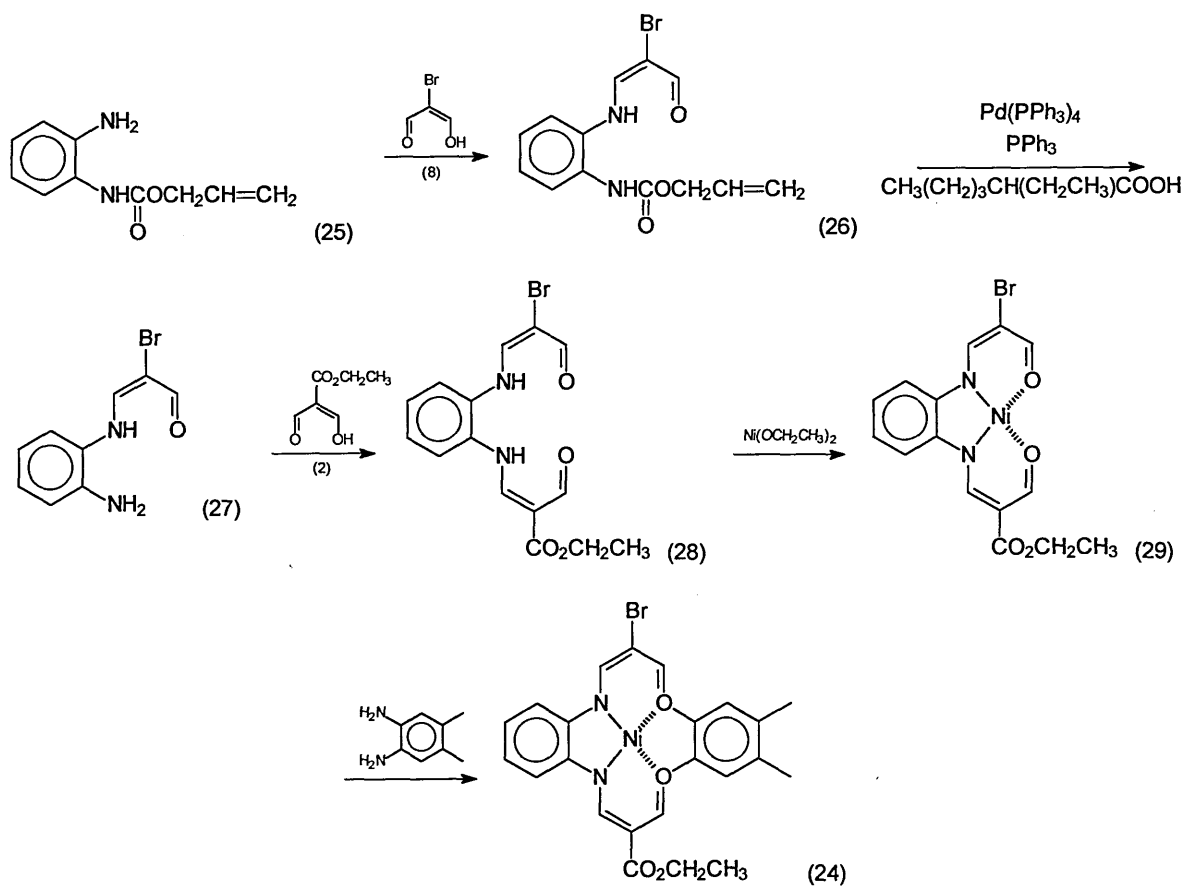
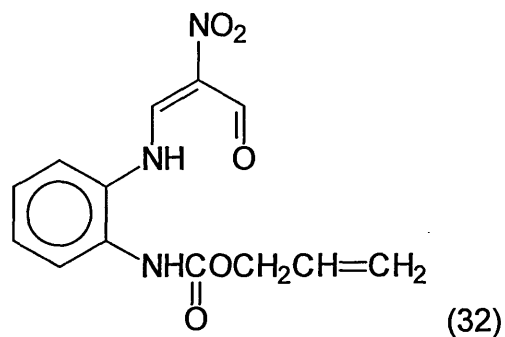


Fig. 3.22

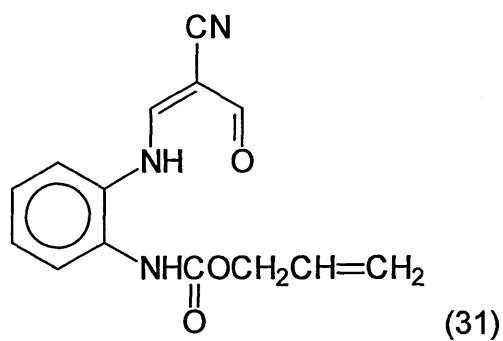
The deprotection of the N-protected mono-anil (26) to the free base (27) was found to be the key stage in the entire synthesis. The deprotection procedure must be very mild as exposure of the free base to any acidic or basic species involved in the deprotection leads to the formation of a symmetrical macrocycle where both propanediiminato bridges are substituted with bromine. A very mild deprotection using 2-ethyl hexanoic acid, triphenylphosphine and tetrakis(triphenylphosphine) palladium(0) in dry ether³³⁵ was performed from which the free base mono-anil (27) crystallised. Condensation with 2-carboethoxymalondialdehyde (2) in refluxing THF was found to produce the bis-anil (28) which could not be induced to react directly with a second diamine. A template procedure was utilised by stirring the substituted ortho-phenylenediamine with Ni(OAc)₂ in methanol, thus allowing incorporation of a nickel ion into the framework to hold the aldehyde functionalities in the correct geometry for condensation with the second diamine in the molten state (Jagers methodology³³⁶). Purification by column chromatography was found to yield the desired product. Mass spectral, ¹H NMR and microanalysis of the isolated brown solid confirmed its identity.

It is clear that it may be possible to extend this synthetic route to provide additional 2-D unsymmetrical macrocycles by varying the functionalities of both the malondialdehyde and diamine moieties. Investigation into the preparation of such compounds was undertaken and led to the isolation of some of the required intermediates. Although an additional macrocyclic material was not isolated due to time constraints it is clear that this technique has great potential for the preparation of additional 2-D unsymmetrical macrocycles.

The preparation of the bis-anil (30) was attempted by refluxing the bromo substituted mono-anil (27) with 2-nitromalondialdehyde (7) in tetrahydrofuran. The isolated brown solid was found to yield a primary amine stretching peak in the infra-red spectrum indicating the presence of unreacted mono-anil. This conclusion was confirmed by TLC. The formation of the nickel (II) complex was attempted as previously detailed by reaction with nickel (II) acetate in methanol but no discernible difference in the TLC of the material could be detected. The lower yield of bis-anil (30), 48%, compared with the initial reaction, 76%, may have influenced the outcome of this reaction.



The formation of the cyano-substituted mono-anil (31) was achieved by condensation of 2-cyanomalondialdehyde (3) with mono-protected ortho-phenylene diamine (25). Two techniques were examined, both involving refluxing the reagents with a catalytic quantity of para-toluenesulphonic acid in either THF or DMF. Both techniques proved to be successful, although refluxing in DMF resulted in improved yield and purity of the product.



An attempt at the deprotection of the DMF prepared mono-anil was undertaken but only resulted in an impure material that confounded any attempts at purification.

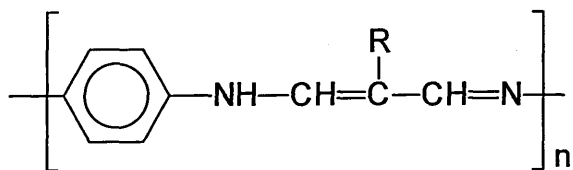
Thus, although success in this initial investigation was somewhat limited, it was shown that the potential exists for the preparation of additional 2-D unsymmetrical macrocycles.

4. Main chain polymers.

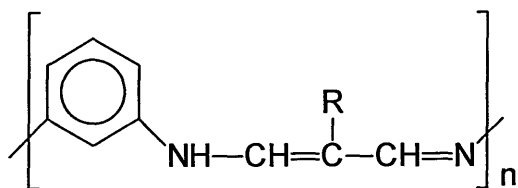
The preparation of main chain polymers has been of interest in respect of liquid crystalline and semiconducting characteristics that may be exhibited. Studies on simple polymers based upon the condensation of meta- and para-phenylenediamine with a series of malondialdehydes have been undertaken, as well as the study of polymers that incorporate a macrocyclic ring system as part of the main chain.

4.1 Schiff base polymers from malondialdehydes/phenylenediamines.

Differing combinations of phenylenediamines and malondialdehydes were condensed to provide Schiff base polymeric materials (Fig. 4.1).



Para-phenylenediamine/malondialdehyde polymer



Meta-phenylenediamine/malondialdehyde polymer

Fig. 4.1 Schiff base polymers.

General Procedures

Method 1 The required malondialdehyde was placed in a three necked round bottom flask and dissolved in dry tetrahydrofuran (10ml.). To this was added para-toluenesulphonic acid and the

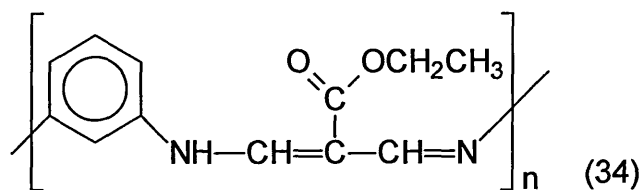
solution brought to reflux under nitrogen. The required phenylenediamine was dissolved in dry tetrahydrofuran (7ml.) and added to the reaction mixture. This was then refluxed for 1 hour under nitrogen after which the solution was cooled and the precipitated solid filtered by vacuum. The crude solid was purified by soxhlet extraction with dichloromethane for 24 hours, after which the product was removed and air dried.

Method 2 The required phenylenediamine was dissolved in dry dimethylformamide (20ml.) along with a catalytic quantity of lithium chloride. To this was added the required malondialdehyde in dry dimethylformamide (10ml.). The reaction mixture was stirred for 24 hours, under nitrogen, in the dark. Upon filtration of the solution a solid was obtained, that was washed with water (1 × 30ml.) and methanol (2 × 30ml.).

Method	Malondialdehyde	Phenylenediamine	Crude yield	Pure yield	Melting point
1	2-Carboethoxy (1.0g, 7mmol.)	Meta- (0.75g, 7mmol.)	0.5g	0.4g	231-234°C
2	2-Carboethoxy (1.0g, 7mmol.)	Meta- (0.75g, 7mmol.)	N/A	0.08g	>340°C
1	2-Carboethoxy (1.0g, 7mmol.)	Para- (0.75g, 7mmol.)	0.91g	0.73g	>340°C
1	2-Bromo (1.0g, 7mmol.)	Meta- (0.71g, 7mmol.)	1.25g	0.95g	>340°C
1	2-Bromo (1.0g, 7mmol.)	Meta- (0.71g, 7mmol.)	1.34g	1.18g	>340°C

Both 2-carboethoxymalondialdehyde and 2-bromomalondialdehyde were examined following the procedures documented (chapter 5). The procedures were essentially one step polymerisation reactions followed by a simple purification. These polymers are analogous to the DBTAA's as they may be considered as open chained forms of the macrocycles themselves.

Of the four main chain polymers produced one in particular proved itself to be of interest (34).

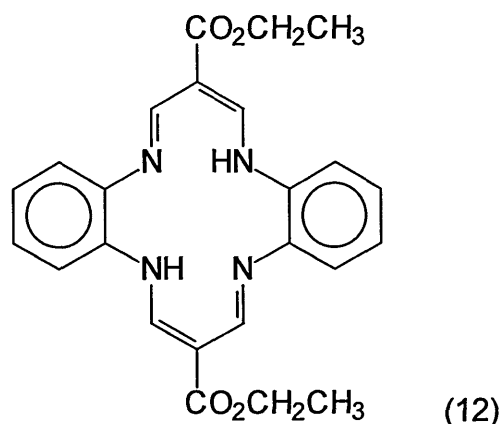


The preparation of this polymer from 2-carboethoxymalondialdehyde and meta-phenylenediamine was examined by two procedures:

- i. Reflux in tetrahydrofuran using a para-toluenesulphonic acid catalyst
- ii. Reflux in dimethylformamide using a lithium chloride catalyst.

The product from these methods not only differed in colour but also in melting point (i. 231-234°C, ii. >340°C). It is also interesting to note that the use of differing reaction conditions appears to have affected parameters such as chain length and degree of crystallinity of the compound.

It is apparent that the polymer is analogous in structure to the macrocyclic compound 6,13-dicarboethoxy-dihydrodibenzo[b,i]tetraazacyclotetradecine (12). A comparison of the IR spectrum of the two materials has shown each to exhibit all the expected major bands. A more detailed analysis of the structure of the two materials by solid state CPMAS ^{13}C NMR spectroscopy was then undertaken in order to more fully explore the functionalities present (spectra are illustrated in appendices 1 and 2). The carbon atoms of the macrocycle itself could be fully assigned. Comparison with the major peaks of the polymer spectra showed considerable peak matching, allowing us to further illustrate the similarity between the two structures. It is interesting to note when examining the spectra of these materials that the chemical shifts of the peaks due to the carbons that form the propanediiminato bridges match perfectly, whilst there is some discrepancy between the peaks corresponding to the phenyl carbons. This may be the fact that there is meta-substitution in the polymer whilst ortho-substitution is present in the macrocycle.

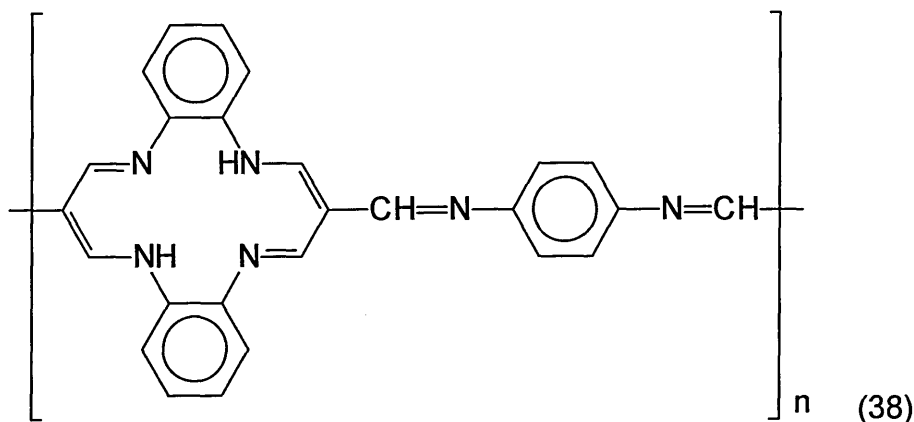


Thermal properties

A study of the thermal properties of the polymer was undertaken and initially appeared to give promising results. A study of the polymer by differential scanning calorimetry (see appendices 4 and 5) indicated that the molecule exhibited a series of exothermic transitions over a temperature range of 300°C which were thought to be due to crystalline ordering. However, thermal gravimetric analysis (see appendix 6) of the material showed a significant weight loss to occur at each of the DSC transitions. It was concluded that a thermal decomposition of the product was occurring.

4.2 Polymeric materials incorporating macrocyclic rings.

The incorporation of planar, macrocyclic rings into an ordered polymeric environment is of interest in the fields of semiconductors and liquid crystals due to the physical characteristics they possess. The preparation of a linear polymer that incorporates a macrocycle into its structure has been attempted by the condensation of 6,13-diformyldihydrodibenzo[b,i][1,4,8,11]tetraazacyclotetradecine and meta-phenylenediamine (38).



These polymeric materials are analogous in structure to the main chain liquid crystalline polymers previously described (chapter 2 sect. 5.1.1). The macrocyclic unit may be thought of as the mesogen whilst the malondialdehyde acts as the linkage molecule. It may therefore be envisaged that this type of molecule may allow crystalline ordering or semi-conducting behaviour.

5. Side chain polymers.

The preparation of macrocyclic side chain polymers, that have the structural requirements that may promote the exhibition of liquid crystallinity or semiconductivity, has entailed the use of some detailed synthetic chemistry.

The concept of molecularly tailoring the structure of polymers to exhibit liquid crystalline or semi-conducting characteristics has already been discussed in detail (chapter 2 and 3). Essentially the synthetic strategy adopted by ourselves was to endeavour to prepare a polymeric chain that incorporated DBTAA rings as pendant side groups (fig. 5.1).

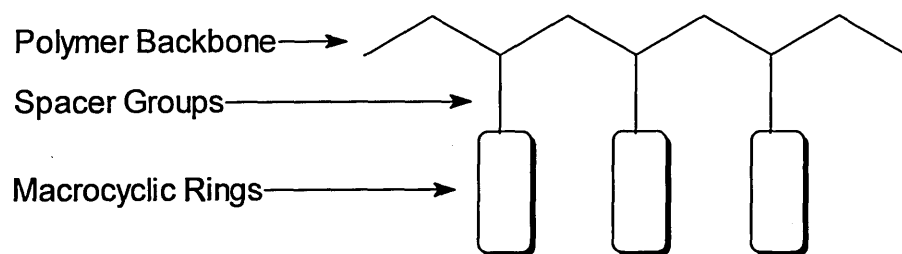


Fig. 5.1 Schematic of a typical side chain polymer.

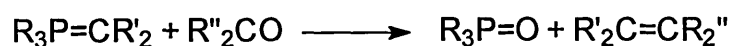
It was conceived that the possibility may exist of attaching a polymerisable group eg. an unsaturated linkage, to the macrocycle. This group may then in turn lead to the side chain polymer by utilising the appropriate polymerisation procedure. The attachment of a polymerisable side chain may itself be further sub-divided in terms of strategy into two categories

1. The polymerisable group is attached to a fully cyclised macrocyclic ring.
2. The polymerisable group is attached to a malondialdehyde unit that is then cyclised with an uncyclised metal chelate.

The approach to this synthetic strategy was to use the Wittig reaction and the Gabriel synthesis.

5.1 The Wittig reaction.

The Wittig reaction³³⁷⁻³⁴¹ has established itself as an important synthetic tool within the field of organic chemistry, and in its simplest terms may be described as the reaction between a phosphonium ylide and an aldehyde or ketone to form an olefin and a phosphine oxide.



The Wittig ylide is generally formed in a two step process that involves the nucleophilic attack by a phosphine on an alkyl halide, followed by the removal of an acidic proton situated on the newly

Our approach to the use of the Wittig reaction in the preparation of a polymerisable macrocycle was to react a suitable triphenylphosphonium iodide (for our purposes 1-pentyl-5-triphenylphosphonium iodide (41)) with the 1-D unsymmetrically substituted formyl macrocycle (6,13-formyl-dihydrodibenzo[b,i][1,4,8,11]tetraazacyclotetradecine (22)) (fig. 5.3).

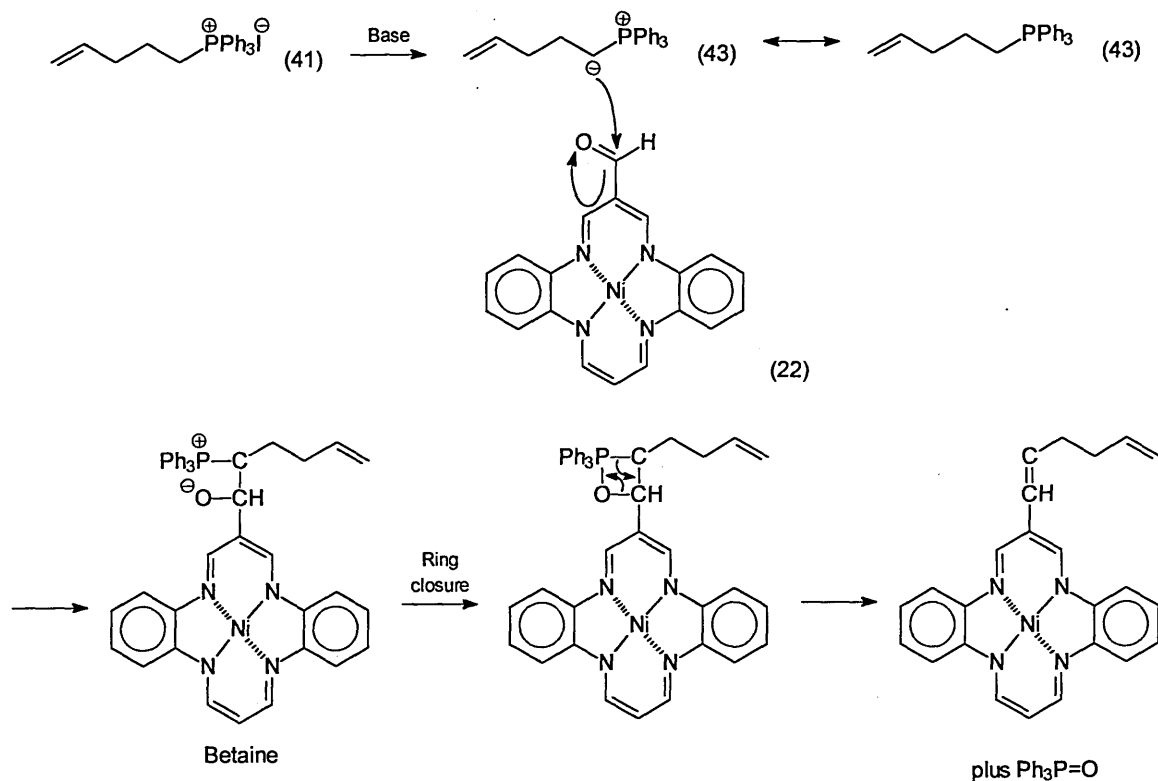


Fig. 5.3 Synthetic strategy

It can clearly be seen from this that the possibility exists for polymerising the terminal alkene group to produce a polyethylene backbone with pendant macrocyclic side groups separated from the main chain by a four carbon chain (fig. 5.4). The length of this chain can be critical if the material is to exhibit liquid crystalline or semi-conducting characteristics. The macrocyclic side groups must be able to become ordered; thus a chain that is too short will constrict the movement of the macrocycles and therefore inhibit ordering, whilst chains that are too long may allow too much free movement which may also have the effect of inhibiting macrocyclic ordering.

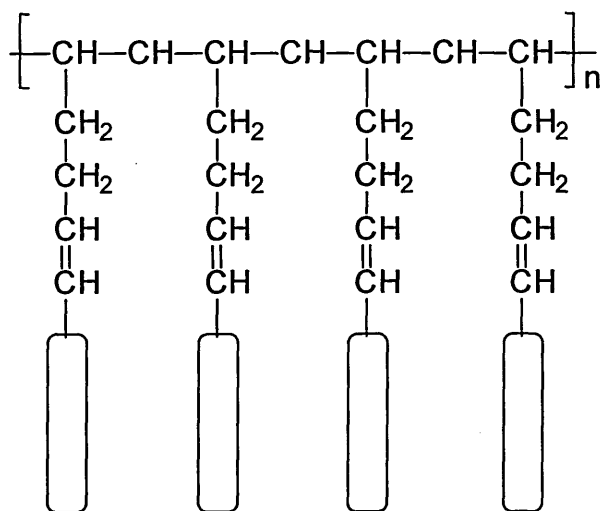
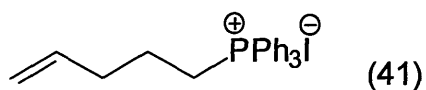


Fig. 5.4 Polymer with macrocyclic side groups

5.1.1 Synthesis

i. Preparation of the quaternary phosphonium salt

The first stage in the attempted synthesis of the macrocyclic side chain polymer was the preparation of the quaternary phosphonium salt 1-pentenyl-5-triphenylphosphonium iodide (41)



The most widely used process leading to phosphonium compounds is the reaction of the trivalent phosphorous with a substance of the general formula RX. R may be an H, an alkyl or an acyl radical whilst X may be a halogen, an acyl radical or an alkoxy substituent. For example esters, ethers or anhydrides can react (fig. 5.5).

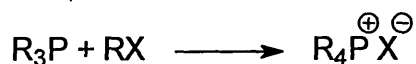
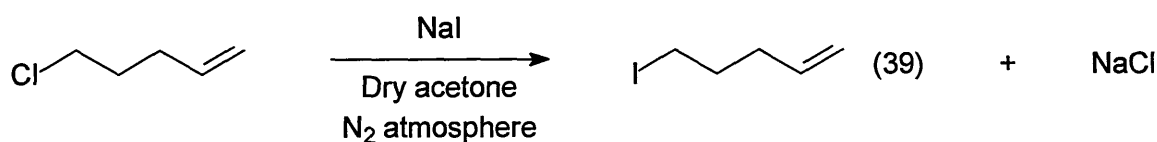


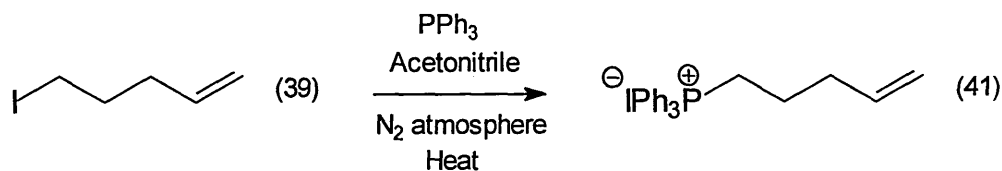
Fig. 5.5

By far the simplest procedure for the preparation detailed above utilises halides as the X substituent. There is however a marked difference in the reactivity of the halides. Iodides are more reactive than bromides, and these in turn are more reactive than chlorides³⁴². It may therefore be understood that the first stage of our synthesis was the conversion of the commercially available 5-chloro-1-pentene to 5-iodo-1-pentene (39).



The procedure involved the reaction of the chloro substituted pentene with NaI to facilitate a transhalogenation reaction which proceeded with a 100% reaction efficiency to yield a yellow solid found to be pure by TLC.

Procedures detailed in the literature³⁴³ enabled the formation of the 1-pentenyl-5-triphenylphosphonium iodide (41) by the reaction of 5-iodo-1-pentene (39) with triphenylphosphine in dry acetonitrile under a nitrogen atmosphere.



The salt was purified by precipitation from dry ether to yield a white solid in 39% yield. Infra-red spectroscopy revealed all the appropriate peaks to be present.

ii. Preparation of the phosphorous ylide of 1-pentenyl-5-triphenylphosphonium iodide (43)

The preparation of phosphorous ylides is generally achieved by the action of bases upon phosphonium salts³⁴⁴ (fig. 5.6).

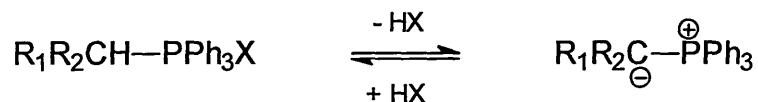
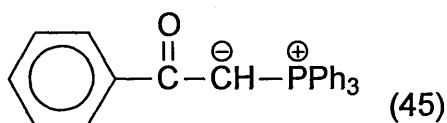
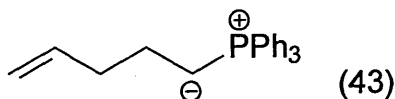


Fig. 5.6 Preparation of phosphorous ylides

The strength of the base necessary to effect deprotonation depends upon the acidity of the phosphonium salt being utilised. For example, the bases placed under investigation for the preparation of the phosphorous ylide of 1-pentenyl-5-triphenylphosphonium iodide (43) were sodium hydride, *n*-butyl lithium and dimethyl sodium whilst the base used for the preparation of the ylide of phenacyltriphenylphosphonium bromide (see later) was sodium carbonate.



The α -hydrogen of (45) is relatively acidic and therefore is easily removed by a less powerful base.

The resulting ylide is also stabilised by resonance with the carbonyl functionality.

The preparation of the required ylide (43) was attempted in three ways. Firstly 1-pentenyl-5-triphenylphosphonium iodide (41) was dissolved in dry tetrahydrofuran under nitrogen. *n*-Butyl lithium was added as the base via a syringe and the mixture stirred for 30 minutes. It should be noted that for this and the following two procedures the ylide was not isolated but used "as is" for reaction with the aldehyde. The success of this stage of the reaction was measured by our ability to make subsequent reactions work.

The next attempted formation of the ylide entailed dissolving the phosphonium salt (41) in dry benzene and stirring with sodium hydride in a dry nitrogen atmosphere for 30 minutes.

The final procedure for ylide formation utilised dimethyl sodium as the base which was prepared by the reaction of dimethyl sulphoxide and sodium hydride (fig. 5.6).

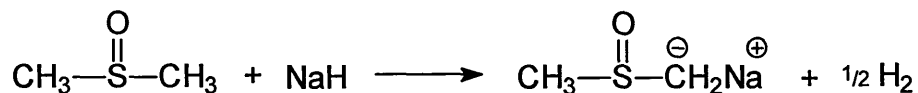


Fig. 5.7 The preparation of dimethyl sodium

The formation of the ylide was attempted by stirring dimethyl sodium with triphenylphosphonium iodide (41) dissolved in dry dimethylsulphoxide under a dry nitrogen atmosphere for 30 minutes. The equations for the procedure are shown below (fig. 5.8).

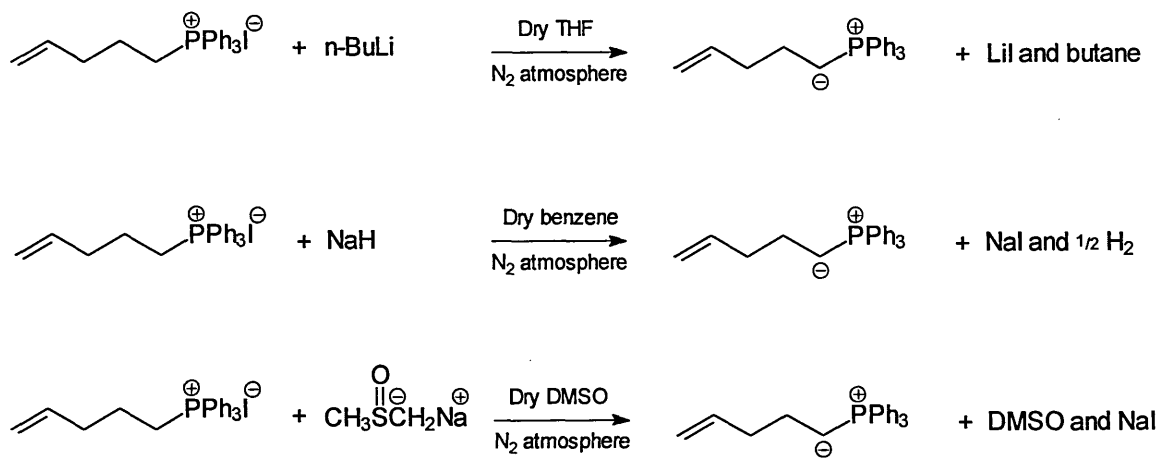
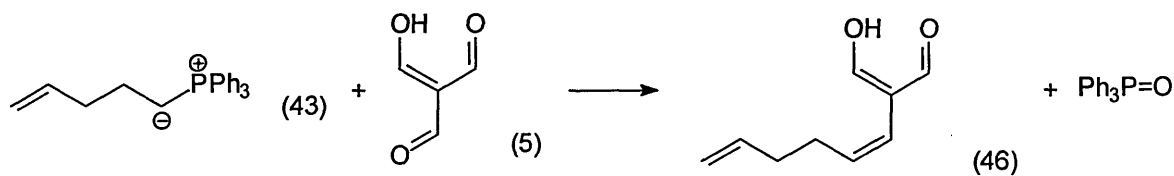


Fig. 5.8 The preparation of the ylide of 1-pentenyl-triphenylphosphonium iodide.

The obvious synthetic stage following the formation of the ylide was its reaction with a suitably substituted malondialdehyde or macrocycle. The former was attempted first by reacting the phosphorous ylides prepared by methods 1 and 2 i.e. those from n-BuLi and NaH, with trimethylmethane in an attempt to produce 2-(1,5-hexadiene) malondialdehyde (46)



The procedure involved stirring the 1-pentenyl-5-triphenylphosphonium ylide solution with trimethylmethane under nitrogen for one hour. TLC of both reaction solutions showed the disappearance of the ylide spot and the occurrence of a new spot which was initially thought to be the Wittig product. However, attempts to isolate the product by solvent extraction with water and dichloromethane were unsuccessful with TLC of the organic layer indicating that reliberation of the phosphonium salt had occurred.

The initial theory that the Wittig product, 2-(1,5-hexadiene)malondialdehyde, had been formed was re-evaluated and found to be open to question. There was the possibility that rather than acting as a nucleophile the ylide was in fact behaving as a base. This would have facilitated the removal of an acidic proton from the trimethylmethane which could indeed be favoured due to the resonance stabilisation which would exist on the resultant enolate ion (Fig. 5.9)

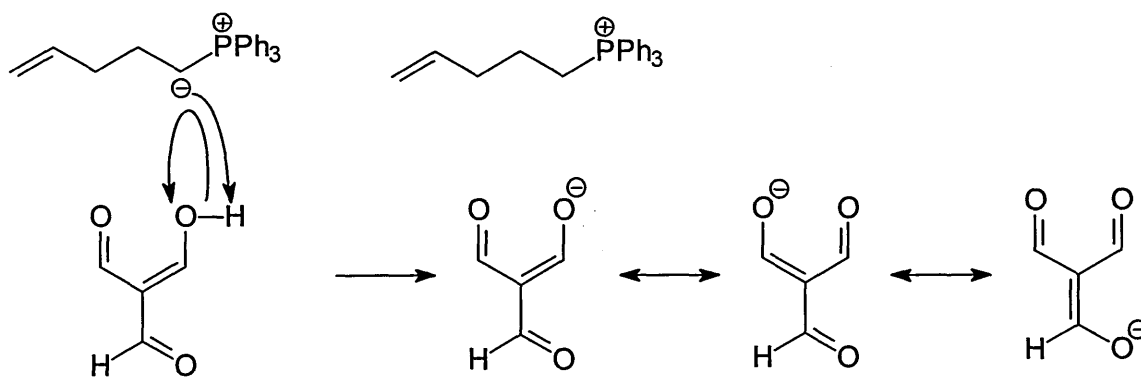
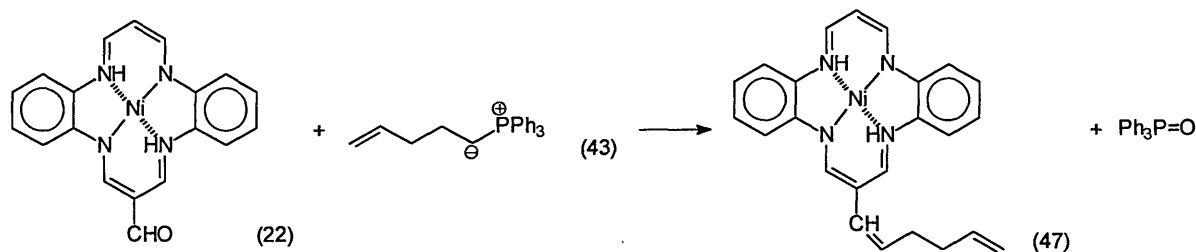


Fig. 5.9 Resonance stabilisation in the trimethylmethane enolate ion

It was identified that potentially the removal of the problem of resonance stabilisation could be achieved by reaction of the appropriate ylide with formyl 1-D unsymmetrical macrocycle (22) to yield

the target molecule 6(1,5-hexadiene)dihydrodibenzo[b,i][1,4,8,11]tetraazacyclotetradecine nickel(II) (47). This procedure was adopted using the phosphorous ylide prepared with dimethyl sodium and the appropriate 1-D unsymmetrical macrocycle which had been purified by soxhlet extraction with dichloromethane.



The reaction was again attempted by stirring for one hour under a nitrogen atmosphere followed by evaporation under reduced pressure. Mass spectral analysis of the resultant solid showed it to be predominately the macrocyclic starting material.

It had become apparent at this stage that under the current set of reaction conditions our target molecule would not be attained. Re-evaluation of the options available to us suggested that the formation of a stabilised phosphorous ylide may have allowed us to consolidate the data and propose a reasonable synthetic approach to the target molecule.

For this purpose two potential halogenated starting materials were selected; benzyl bromide and phenacyl bromide. The use of benzyl bromide shall be discussed first.

Stabilised phosphorous ylide from benzyl bromide

The formation of the stabilised ylide of benzyltriphenylphosphonium bromide (44) was approached by initially producing the phosphonium salt of benzyl bromide (40) by refluxing benzyl bromide with triphenyl phosphine in dry toluene for two hours under a nitrogen atmosphere. The resulting white solid was washed with dry ether before being air dried (fig. 5.10).

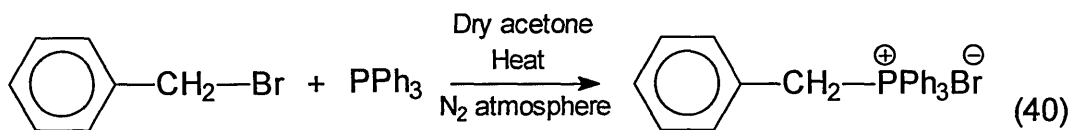


Fig. 5.10 Formation of benzyltriphenylphosphonium bromide

Preparation of the ylide of the phosphonium salt was attempted by reaction with the ethoxide anion formed by the reaction of sodium with dry ethanol in a dry nitrogen atmosphere for 30 minutes (fig. 5.11). The material was not isolated but used as-is for the next stage.

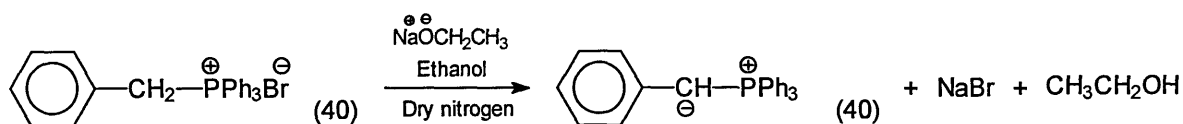


Fig. 5.11 Formation of the benzyltriphenylphosphonium ylide

The ethanolic ylide was reacted with triformylmethane in an attempt to produce 2-(2-phenylethyl-1-ene)malondialdehyde (48). The resultant solution was examined by TLC and found to contain the product spot in addition to triphenylphosphine oxide (a side product of the Wittig reaction. Since the validity of the reaction scheme had now been proven and attention was switched to the preparation of the stable ylide of phenacyltriphenylphosphonium bromide (45)

Stabilised ylide from phenacyl bromide

The preparation of the stabilised ylide of phenacyltriphenyl phosphonium bromide (42) was approached in much the same way as benzyltriphenylphosphonium bromide, but by three different methods. Initially triphenylphosphine and phenacyl bromide were refluxed in a dry nitrogen atmosphere for 1½ hours to yield the phosphonium salt which was precipitated from ether and air dried. The isolated solid was examined by mass spectrometry which indicated the presence of the

expected molecular ion. However, an examination of the ^{31}P NMR spectra revealed the presence of two different phosphorous environments at chemical shifts of δ 22 and δ 42.

5.2 The Gabriel synthesis of amines.

The Gabriel synthesis of amines might be used as a method for the preparation of a macrocyclic side chain polymer, although as will be discussed later the complete synthetic procedure to such a molecule was not attained. As for the Wittig reaction the attachment of a polymerisable side chain to a macrocycle may be approached by-

1. Direct reaction with a suitable macrocycle, or,
2. Reaction with a suitably functionalised malondialdehyde which is then used to cyclise a part formed macrocyclic complex.

The target molecule of the synthetic procedure was 11-aminoundec-1-ene (59). It may be seen that this molecule may react with the aldehyde group of either triformylmethane or the 1-D unsymmetrically substituted macrocyclic complex (22) via a Schiff base condensation to produce a side chain macrocyclic monomer of the type previously discussed.

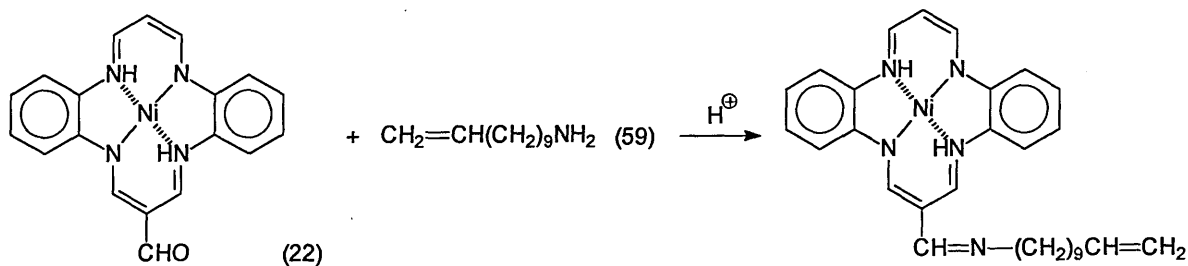


Fig. 5.12 The preparation of the side chain macrocyclic monomer

11-Aminoundec-1-ene was commercially unavailable and therefore a suitable synthesis had to be determined. Our approach was to use the Gabriel synthesis of amines from appropriate starting materials.

The preparation of primary amines may be achieved in good yield by the application of the Gabriel synthesis³⁴⁵. The method involves the alkylation of phthalimide (a protected form of ammonia), which itself is prepared from ammonia and dicarboxylic phthalic acid. The imides, of which phthalic acid (Fig. 5.13) is a member, have acidic properties because the negative charge on the conjugate base can be delocalised over both oxygens and the nitrogen. In aqueous basic solution the compound is converted almost completely to the anion.

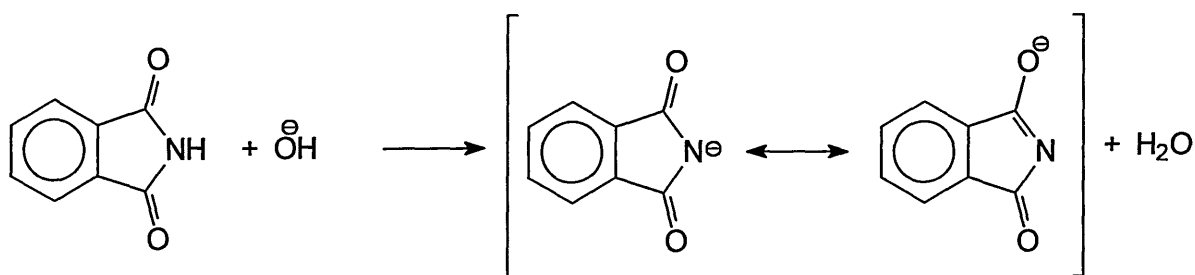


Fig. 5.13 Anion formation of phthalimide.

The phthalimide anion exhibits nucleophilic properties and may enter into displacement reactions with suitable molecules, such as alkyl halides (Fig. 5.14). In theory, reaction may occur at either the oxygen or the nitrogen, but due to the higher nucleophilicity of the nitrogen atom it is the favoured site. The product of the reaction is an N-alkylphthalimide, and the hydrolysis product of this molecule is the amine and phthalic acid.

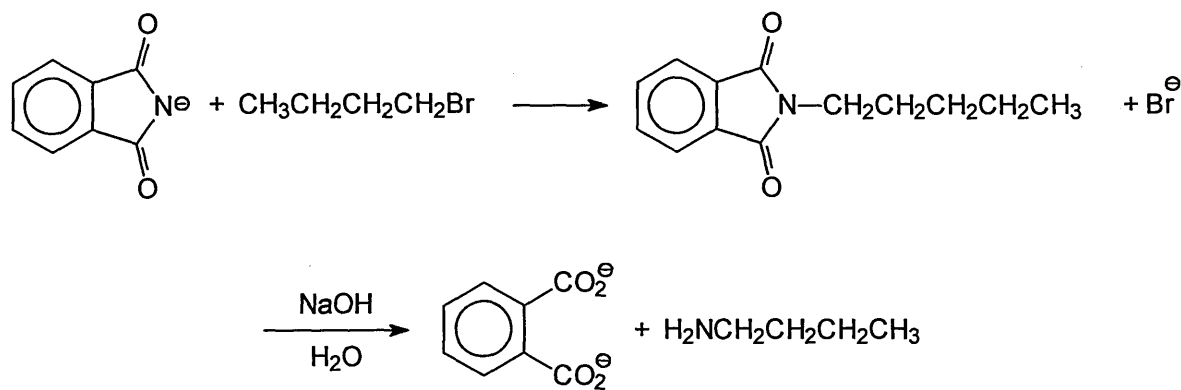


Fig. 5.14 Gabriel synthesis of primary amines.

One of the major benefits of this synthesis is the absence of contamination by secondary and tertiary amines. The reaction may be slow but can be speeded up by the use of dipolar aprotic solvents such as dimethylformamide^{346,347} or with the application of a crown ether³⁴⁸. However, hydrolysis procedures, whether acid or base catalysed is generally slow and more efficient procedures are available. An example of this is the Ing-Manske³⁴⁹ procedure (Fig. 5.15), in which the phthalimide is heated with hydrazine in an exchange reaction with hydrazine to produce the product amine and phthalhydrazide.

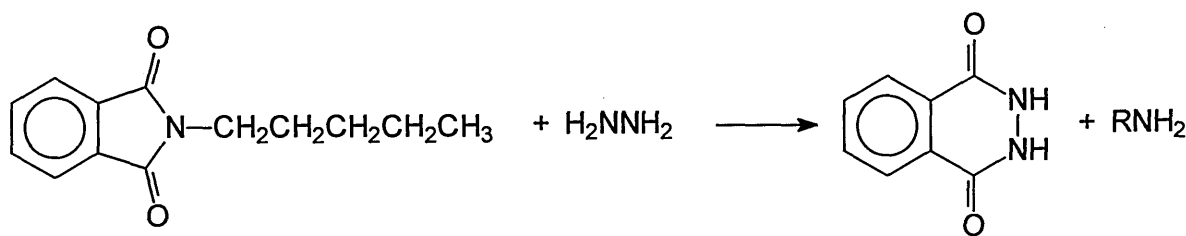


Fig. 5.15 Ing-Manske procedure.

Initial experiments were centered around the examination of the use of the Gabriel synthesis for the conversion of bromoalkanes of varying chain length to the corresponding amine in order to confirm our ability to produce amines by this method.

1-Bromopentane was found to yield the corresponding N-pentylphthalimide (51) when heated with potassium phthalimide in Dimethylformamide (fig. 5.16).

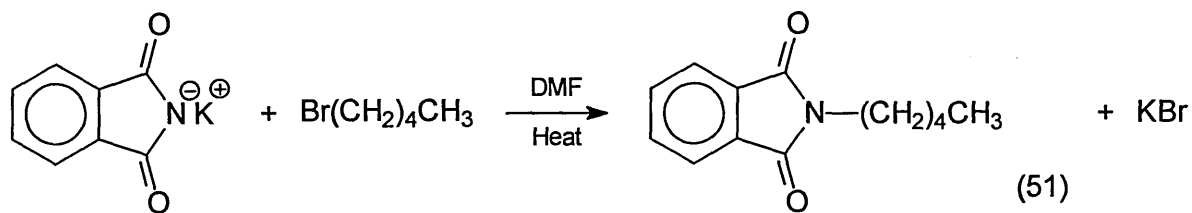


Fig. 5.16 The preparation of N-pentylphthalimide

Liberation of the expected 1-pentamine (57) was achieved by reaction of N-pentylphthalimide with hydrazine monohydrate in refluxing methanol under a nitrogen atmosphere for one hour (fig. 5.17)

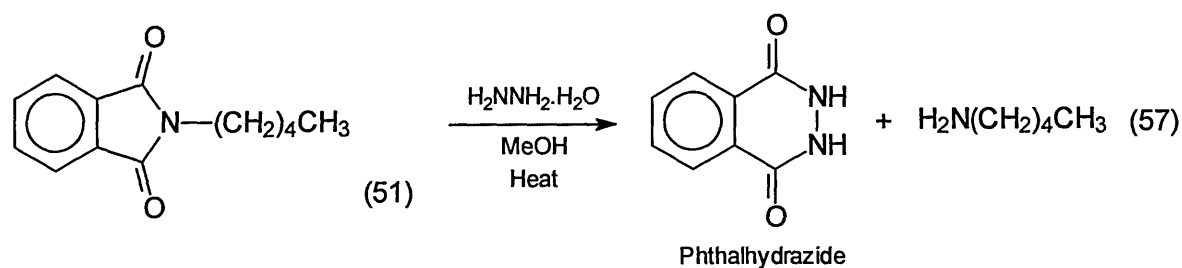
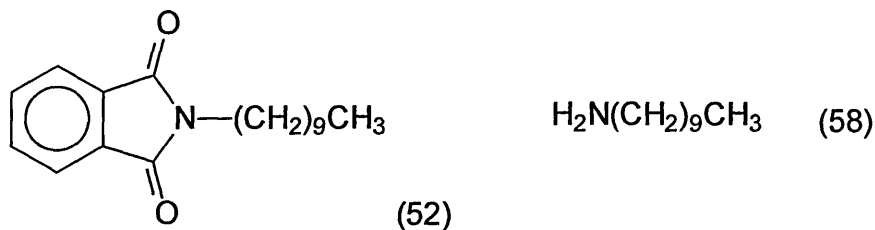


Fig. 5.17 The preparation of 1-pentamine

This initial study into the potential for using the Gabriel synthesis proved to be good. A further study into the effect of increasing the chain length of the initial bromoalkane was undertaken using 1-bromodecane. Reaction procedures were identical to that used for 1-bromopentane, which firstly enabled the isolation of a white solid that was found to be the expected N-decylphthalhydrazide (52) (mass spectra corresponded to that expected). Continuation of the reaction procedure resulted in the liberation of the expected 1-decylamine (58) which was also found to conform to mass spectral analysis.



Isolation of 1-decylamine was found to be somewhat more difficult than for 1-pentamine as it was found to adsorb onto the surface of the crystals of phthalhydrazide side product. Solvent extraction with chloroform and water was found to be the most effective purification technique, but problems were still encountered due to the formation of a soapy layer at the solvent interface presumably due to the presence of the 1-decylamine cation (fig. 5.18).

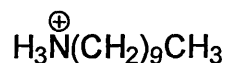


Fig. 5.18

After basifying the product and evaporation of the chloroform a clear liquid was isolated which conformed to mass spectral and infra-red scrutiny. The mass spectra was found to clearly show the subsequent alkyl fragments from the break down of the molecule.

The selected starting material on which the Gabriel synthesis was performed was 11-bromo-undec-1-ene (fig. 5.19), a long chain molecule with terminal allyl and bromo groups.

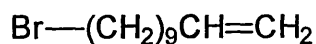


Fig. 5.19

However, this material (or others like it) were commercially unavailable or extremely expensive. With this in mind attempts were made to prepare the material from the appropriate reagents.

The method utilised for the preparation of 11-bromoundec-1-ene involved conversion of the 11-hydroxy derivative using the sulphonate ester approach. The hydroxyl group of 11-hydroxyundec-1-

ene may not be substituted directly by the bromide ion due to its inability to behave as a good leaving group. Conversion of the hydroxy group to the sulphonate ester (54) by reaction with para-toluenesulphonyl chloride in the presence of pyridine was found to facilitate an S_N2 attack by the bromide ion producing the required 11-bromoundec-1-ene (55) (fig. 5.20)

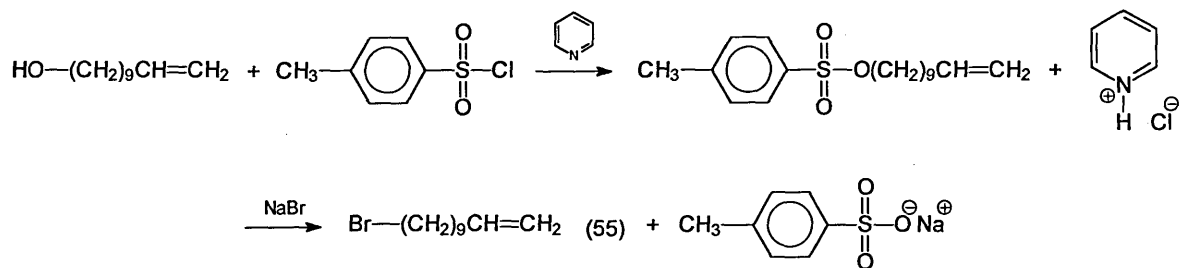


Fig. 5.20

The initial formation of the sulphonate ester was first of all examined on the shorter chain length 1-hexanol and was found to be successful, resulting in the isolation of a clear liquid with a 74% yield. The mass spectra of the material was found to conform with the expected result. Transfer of the technique to 11-hydroxyundec-1-ene necessitated the use of solvent extraction with 2M hydrochloric acid to facilitate the removal of pyridinium hydrochloride. An additional purification on a silica column was required to yield the product, 10-undecenyl-para-toluenesulphonate (54) as a colourless liquid that was also found to conform to the expected mass spectral result.

Nucleophilic attack of the sulphonate ester with a bromide ion was attempted in two ways.

The first utilised sodium bromide in refluxing tetrahydrofuran to produce a milky solution which upon filtration through celite was found to yield 11-bromo-undec-1-ene (55) as a colourless liquid that agreed with mass spectral analysis.

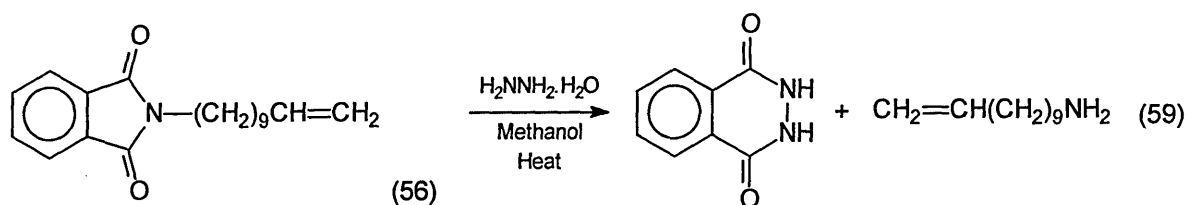
The second method utilised the same conditions but used tetra-n-butylammonium bromide as a replacement for sodium bromide. The resultant N-butylammonium tosylate was removed from the sample by solvent extraction resulting in the isolation of 11-bromo-undec-1-ene (55) as a pale yellow

liquid. Analysis of the liquid by mass spectrometry and ^1H NMR spectroscopy agreed with the expected data.

Both of the samples from the above two methods were found to give the same products in further reactions.

The Gabriel synthesis described earlier afforded the expected N-undec-1-enylphthalimide (56) which was purified by solvent extraction with chloroform, 2M sodium hydroxide and water before evaporation of the organic layer to a volume of approximately 10 mls before a final wash with saturated brine to remove residual dimethylformamide.

Complete evaporation of the chloroform produced a yellow solid that solidified to an off-white powder upon cooling. Mass spectral and ^1H NMR examination of the product showed it to be slightly contaminated with DMF.



11-Aminoundec-1-ene (59) was liberated from N-undec-1-enylphthalimide as previously discussed.

The precipitated phthalhydrazide crystals were isolated and extracted with petrol under soxhlet extraction for 24 hours. Evaporation of the soxhlet layer gave the required product as a pale yellow liquid that conformed with mass and infra-red spectra.

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Research Study Programme

As part of this project the author has attended various research colloquia given by both internal and external speakers at Sheffield University, Sheffield Hallam University, and during a seconded period at Ohio University, Athens, Ohio, USA.

The author has attended symposia on:

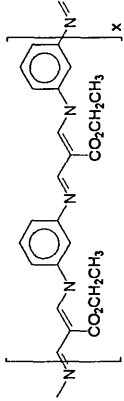
Stereochemistry	Sheffield - 1990, 1991, 1992
Organic chemistry	Nottingham - 1991, Loughborough - 1993
Polymer chemistry	Cincinnati, USA - 1992

The author has presented a poster at the RSC organic chemistry symposium, Loughborough - 1993.


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Rick Challener
Operator Cathy Sultany
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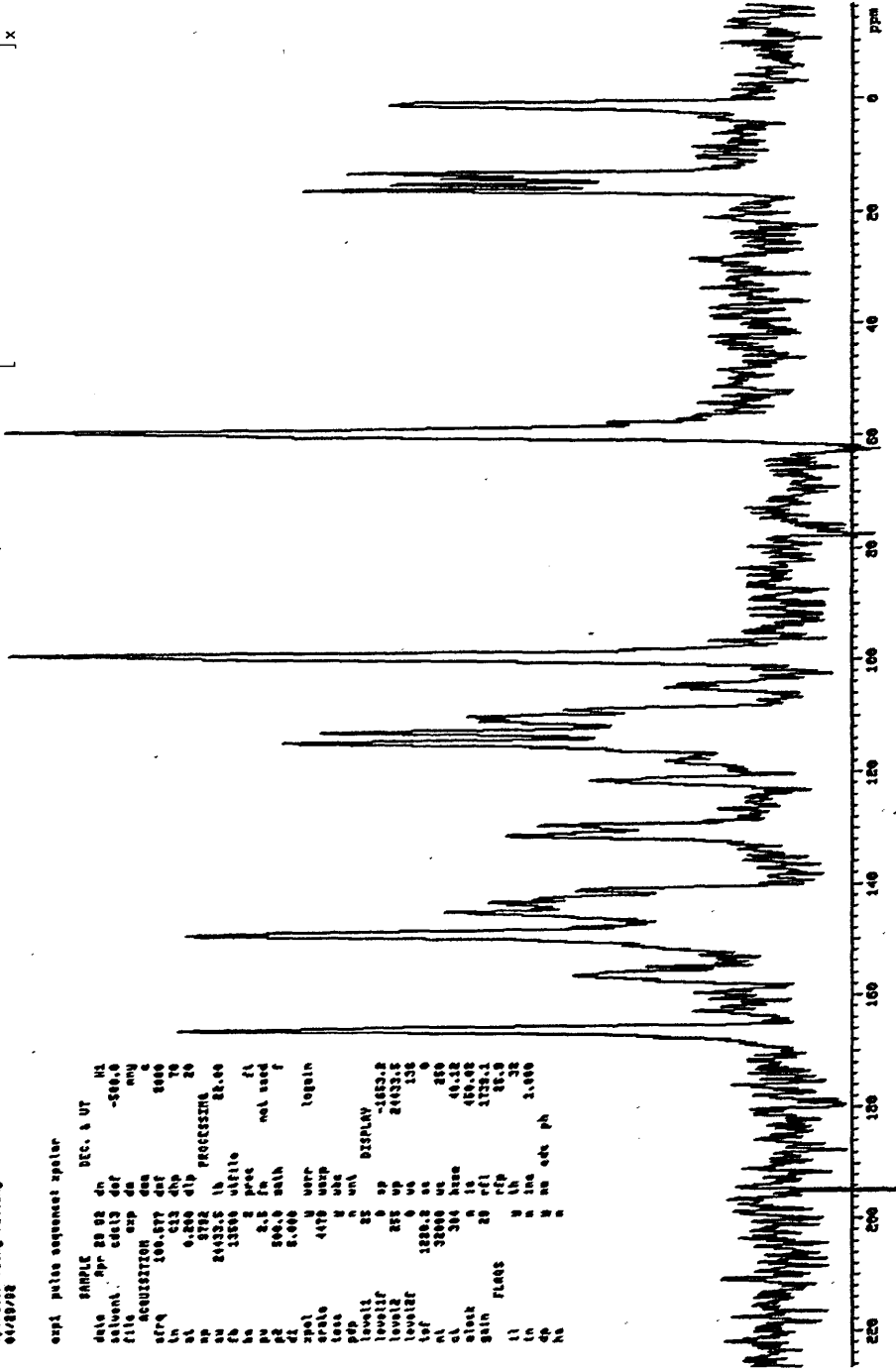
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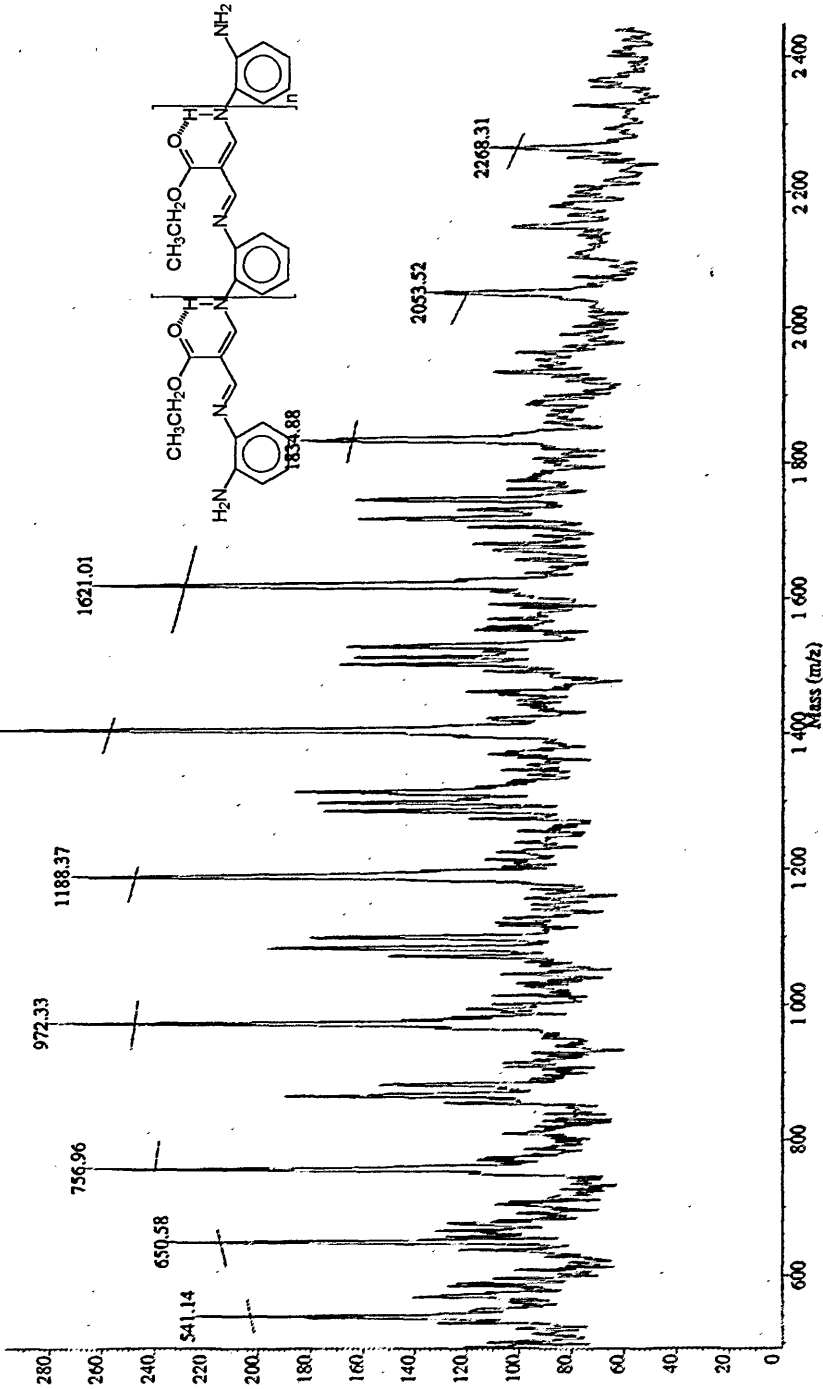
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Appendix 2 – ¹³C CP/MAS NMR spectra of the Schiff base polymer from 2-carboethoxymalondialdehyde and meta-phenylenediamine

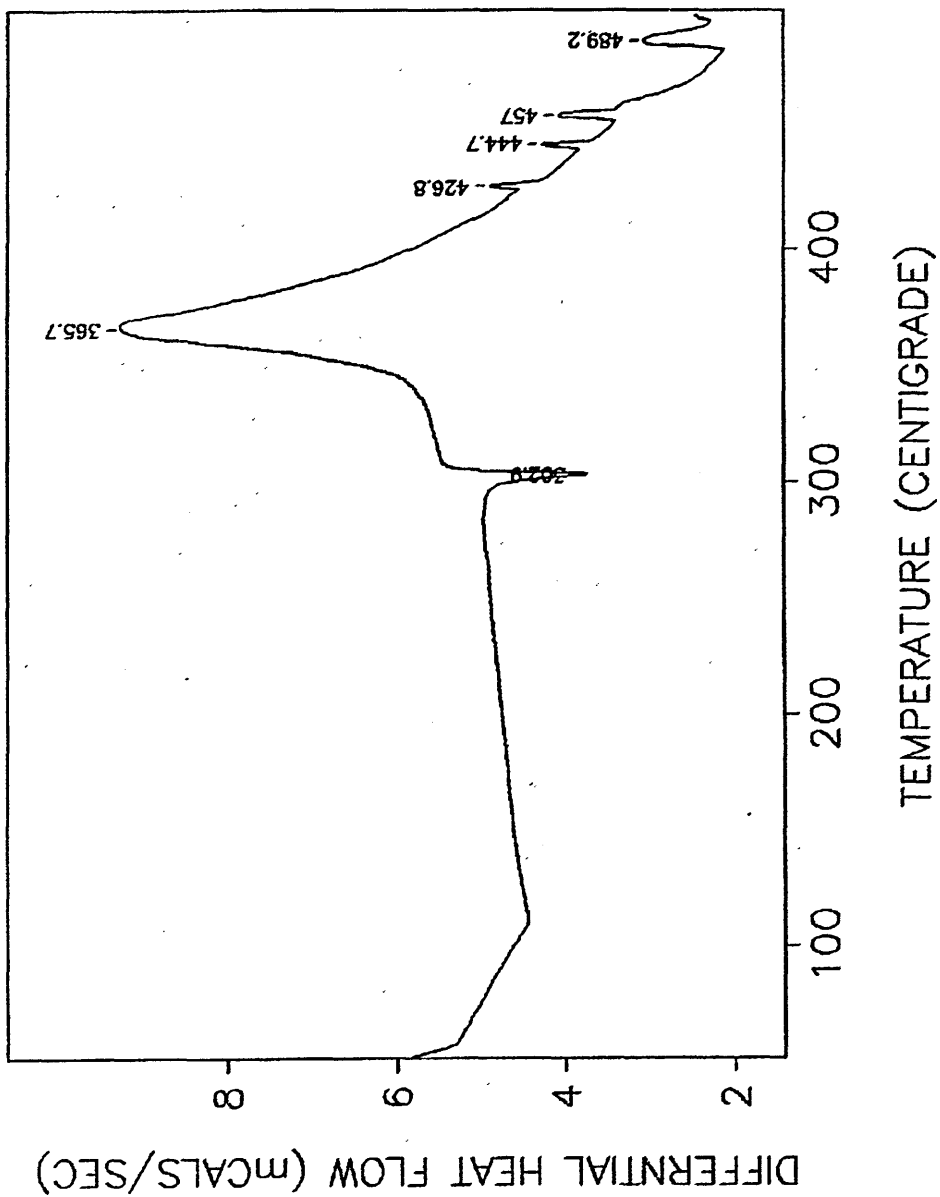
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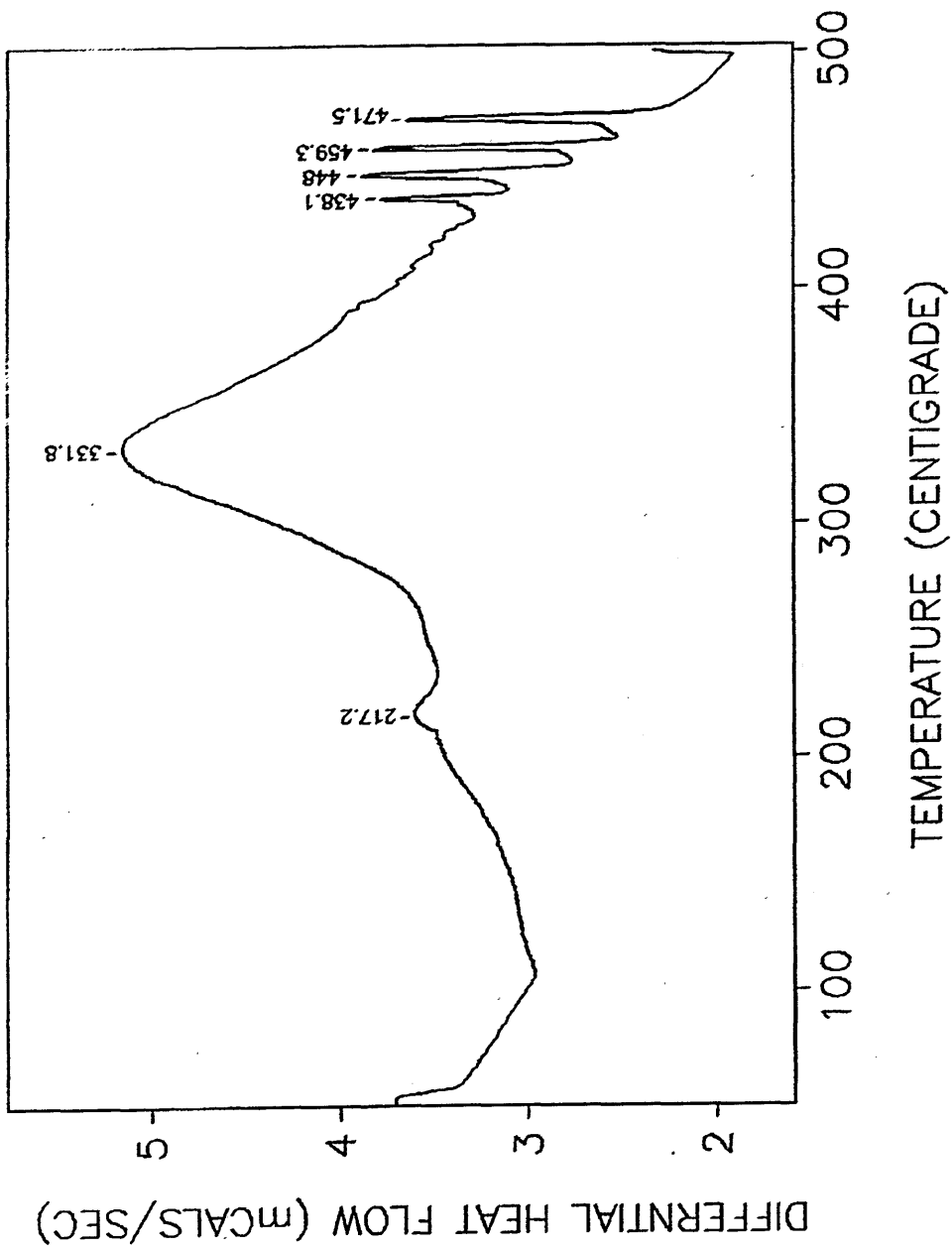


Appendix 3 – MALDI-TOF Mass spectra of the Schiff base polymer from 2-carboethoxymalondialdehyde and ortho-phenylenediamine

DI-CARBOETHOXY MACROCYCLE (1st Heat)



Appendix 4 – Differential scanning curve of 6,13-dicarboethoxydihydrodibenzo[b,1][1,4,8,1]tetraazacyclotetradecine

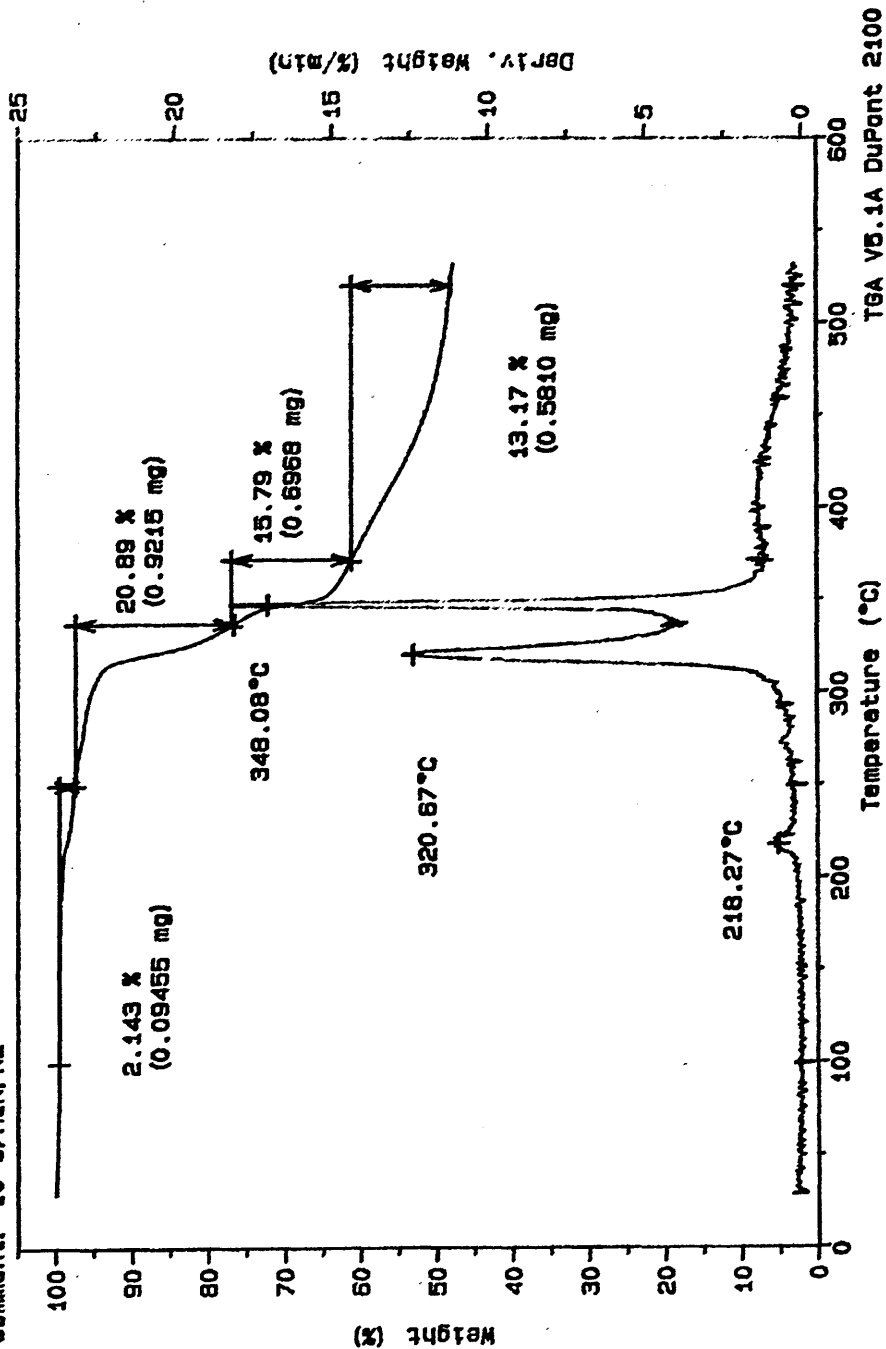


Appendix 5 – Differential scanning calorimetry curve of the Schiff base polymer from 2-carboethoxymalondialdehyde and meta-phenylenediamine

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Size: 4.4120 mg
Method: L.C. POLYMERS
Comment: 10 °C/MIN, N2

TGA

File: C: TGA0887.01
Operator: WEISSMAN
Run Date: 27-May-92 09:59



Appendix 6 - Thermal gravimetric analysis of the Schiff base polymer from 2-carboethoxymalondialdehyde and meta-phenylenediamine