

**THE SYNTHESIS OF NOVEL PORPHYRIN  
MACROCYCLES FOR THEIR USE AS POTENTIAL  
NON-LINEAR OPTICAL MATERIALS**

A Thesis submitted for the degree of Doctor of Philosophy

by

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## **ABSTRACT**

The potential organic molecular compounds exhibit for the use as non-linear optical materials, has received a lot of attention recently. Aromatic compounds containing extensive delocalised  $\pi$ -electronic systems are of particular interest. Porphyrins and metalloporphyrins contain an extensive delocalised  $\pi$ -electron system and are amongst those compounds of interest. The ability to manipulate the porphyrins peripheral substitution pattern has led to the synthesis of a range of novel porphyrin macrocycles. A series of meso- substituted porphyrin macrocycles has been synthesised and the non-linear optical properties of these compounds screened.

The synthesis of a series of symmetrical meso- substituted porphyrins was achieved by the reactions of various aldehydes with pyrrole or a dipyrromethane. The synthesis of a series of unsymmetrical porphyrins was achieved by the mixed condensation of two benzaldehydes and pyrrole and also by reactions at the periphery of the symmetrical porphyrins.

The Reverse Saturable Absorption properties of the synthesised porphyrins was tested and was exhibited by a number of these compounds.

The RSA properties of the compounds were enhanced on the introduction of an unsymmetrical nature to the macrocycle. Also, the effect is enhanced when the ethynyl moiety was introduced to the porphyrins periphery. This is due to the greater overlap between the macrocycle and the peripheral substituents.

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# 1 INTRODUCTION

## 1.1 Review

All life on this planet relies directly on the control role played by porphyrins. Nature has found a prominent place for porphyrins and related macrocycles including reduced porphyrins such as chlorins and bacteriochlorins. Porphyrins have several important biochemical functions including oxygen and electron transport and storage (haemoglobin, myoglobin), electron transfer (cytochromes) and biocatalysis (catalase, peroxidase). More recently attention has been focused on the ability of certain porphyrins to localize in tumour cells, coupled with its photosensitizing properties in the novel treatment of malignant tissues. With this increased interest in porphyrins and metalloporphyrins from chemists of diverse backgrounds, the need to access variously substituted porphyrins has escalated enormously. This introduction gives an insight into the central role played by porphyrins and metalloporphyrins and how construction and manipulation of substitution on the macrocycle's periphery produces compounds that have a novel biochemical and chemical importance.

## 1.2 Nomenclature

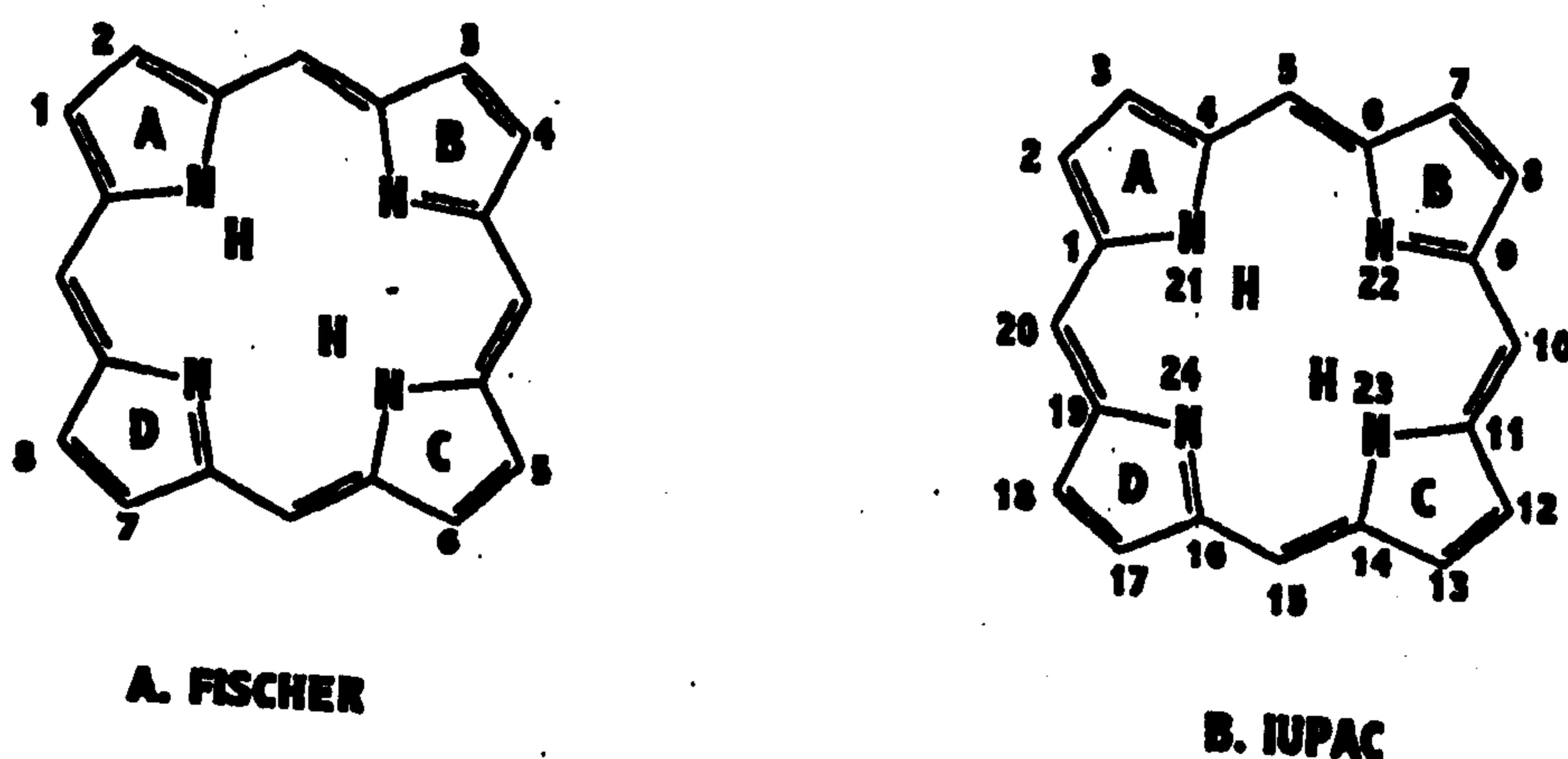


Figure 1.1

### 1.2.1 Fischer Nomenclature

The porphyrin nucleus is a cyclic tetrapyrrolic system consisting of a 20-carbon skeleton. The system consists of four pyrrole nuclei linked by single carbon atom bridges resulting in a macrocycle with complete conjugation of double bonds.

The original porphyrin nomenclature was developed by Hans Fischer<sup>(1)</sup> in the 1920's and was based on the basic ring structure, porphin (A). Fischer adopted a numbering system whereby the pyrrolic ( $\beta$ ) positions are numbered 1-8 and the bridging (meso) positions named  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$ . In an attempt to distinguish isomeric possibilities, Fischer adopted a "type isomer" system employing a Roman numeral nomenclature to distinguish the isomeric types. For a system consisting of two different substituents located on the  $\beta$ -positions of the pyrrole rings, there are four possible isomers (Figure 1.2).

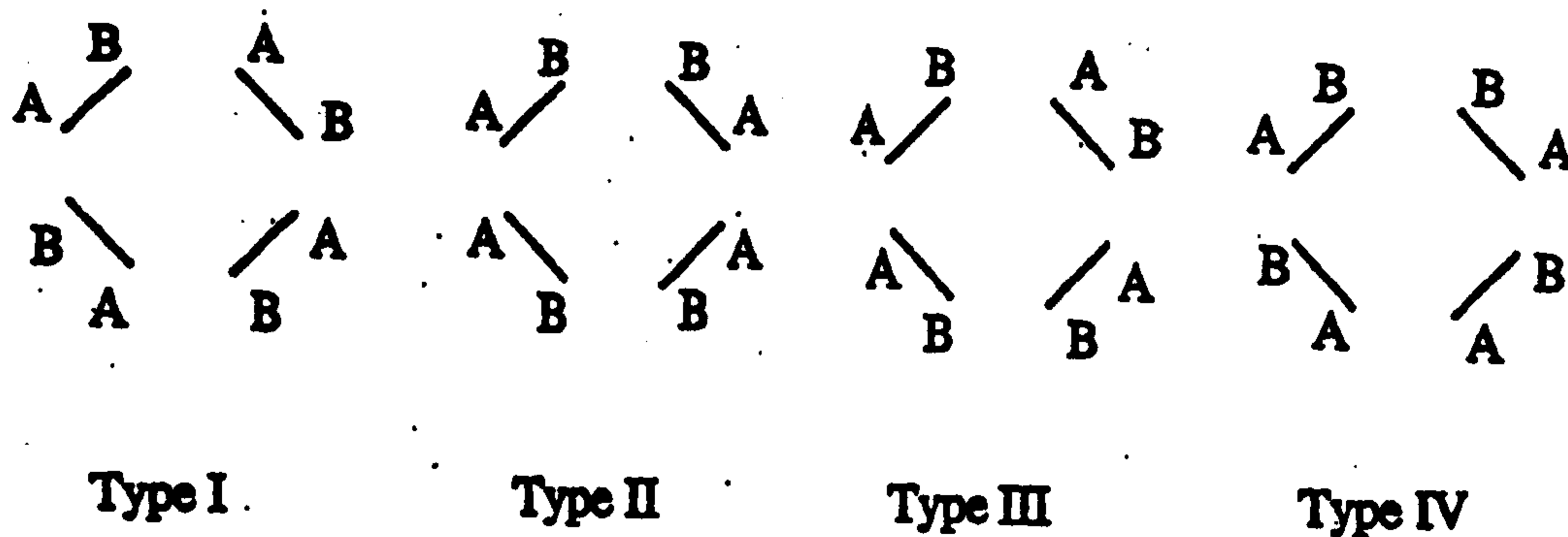


Figure 1.2

For the substitution pattern where three different substituents are employed, the number of isomers increases to fifteen. On subsequent additions of substituents to the porphyrins periphery, the complexity of isomers increases and on four and five substituents the number of isomers increases to 24 and 96 respectively.

Fischer's nomenclature relies heavily on a large number of trivial names based on the substituents, and unfortunately relays little or no structural information. The inability of the Fischer system to name a large number of newly isolated

and synthetic porphyrins led to the intervention of the Joint Commission of the International Union of Pure and Applied Chemistry (IUPAC) and the International Union of Biochemistry (IUB)<sup>(2)</sup> to introduce a new system. This was based on a systematic nomenclature and featured a 1-24 numbering system.

### 1.2.2 IUPAC Nomenclature

The IUPAC system is based on a 1-24 numbering system (B). The parent macrocycle is called porphyrin, a name originally used by Hoppe-Seyler.<sup>(3)</sup> The system is based on the numbering of all the ring positions, including nitrogen, and the individual rings denoted by letters A, B, C and D. The different positions on the ring are now labelled as follows: the  $\alpha$ -positions are represented by the numbers 1,4,6,9,11,14,16,19, the  $\beta$ -pyrrolics 2,3,7,8,12,13,17,18 and the meso-positions 5,10,15 and 20. The central nitrogens are then labelled 21,22,23 and 24. The IUPAC system also takes into consideration the labelling of side chains on the porphyrin's periphery (Figure 1.3).

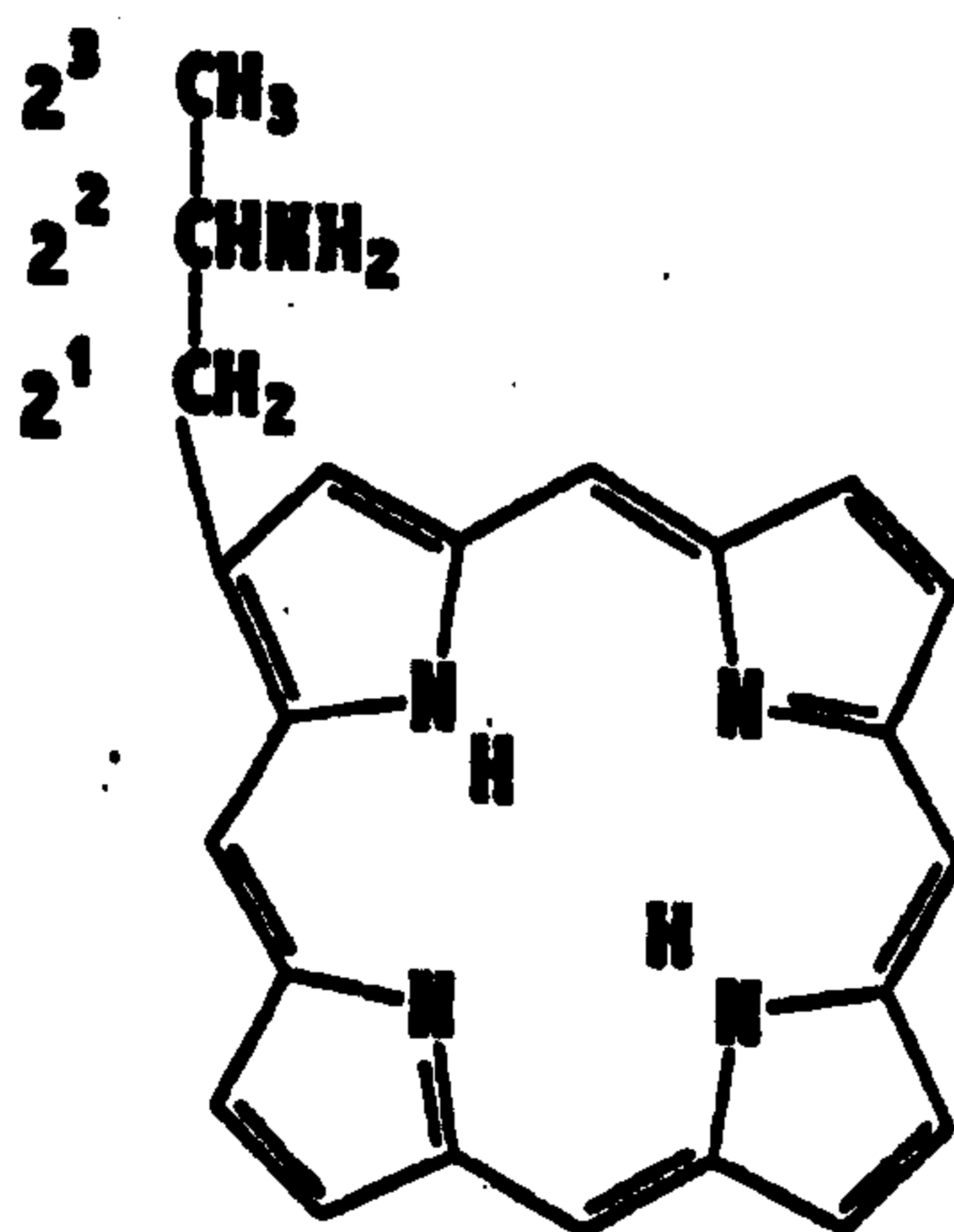
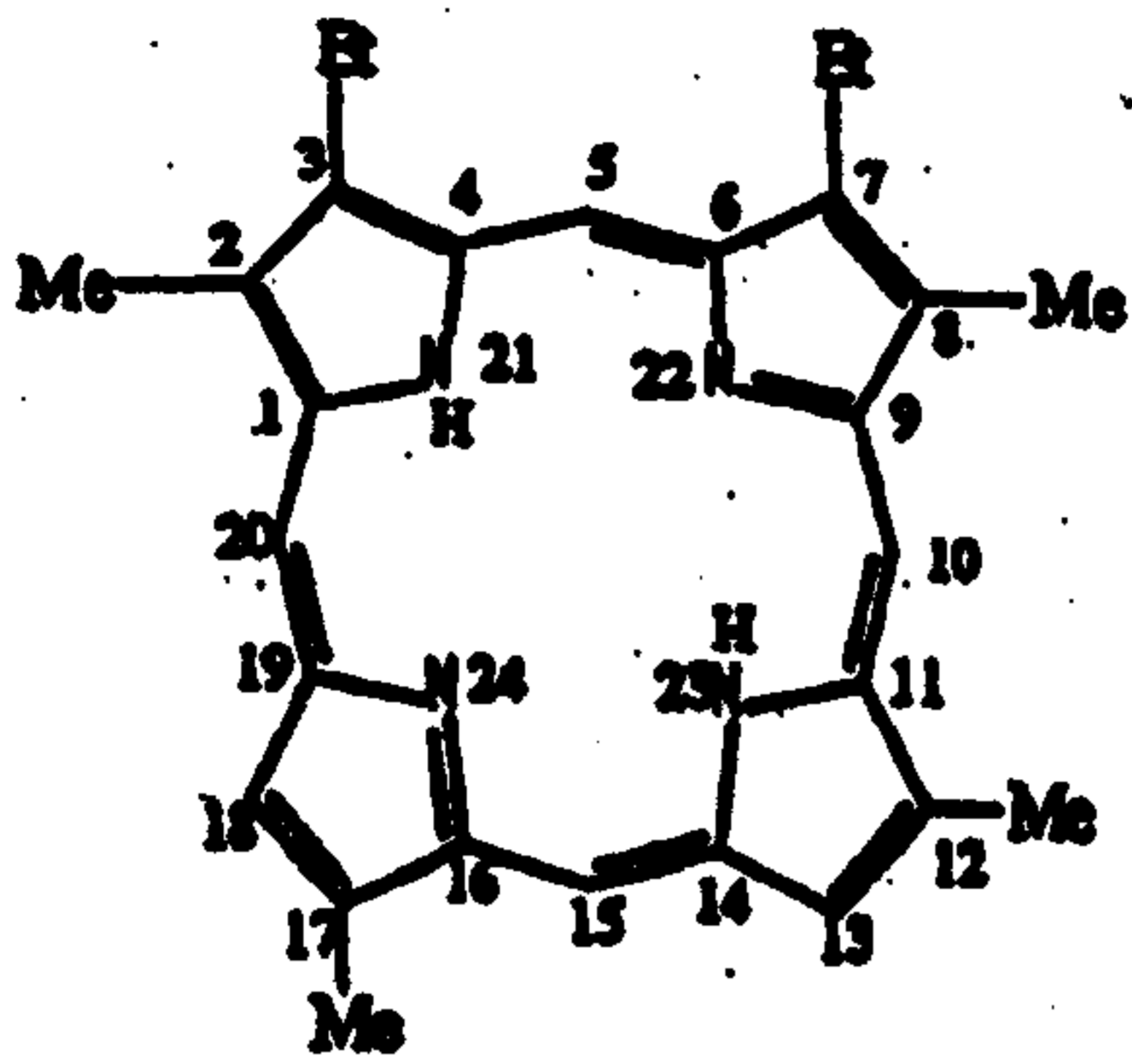


Figure 1.3



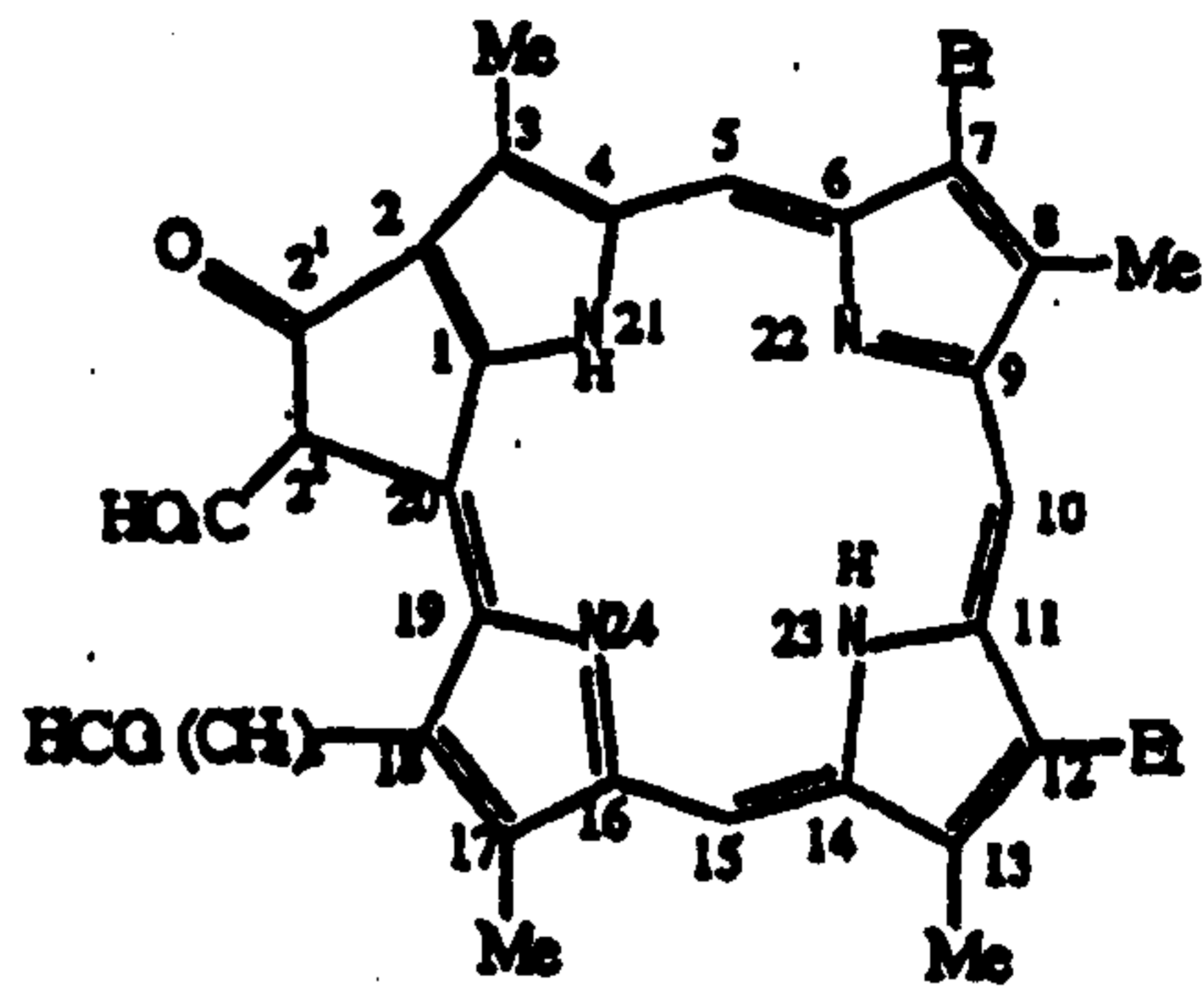
A selection of examples of the nomenclature represented by both Fischer and IUPAC are represented in Figure 1.4.



Fischer: Deuterioetio porphyrin IX

Systematic Name:

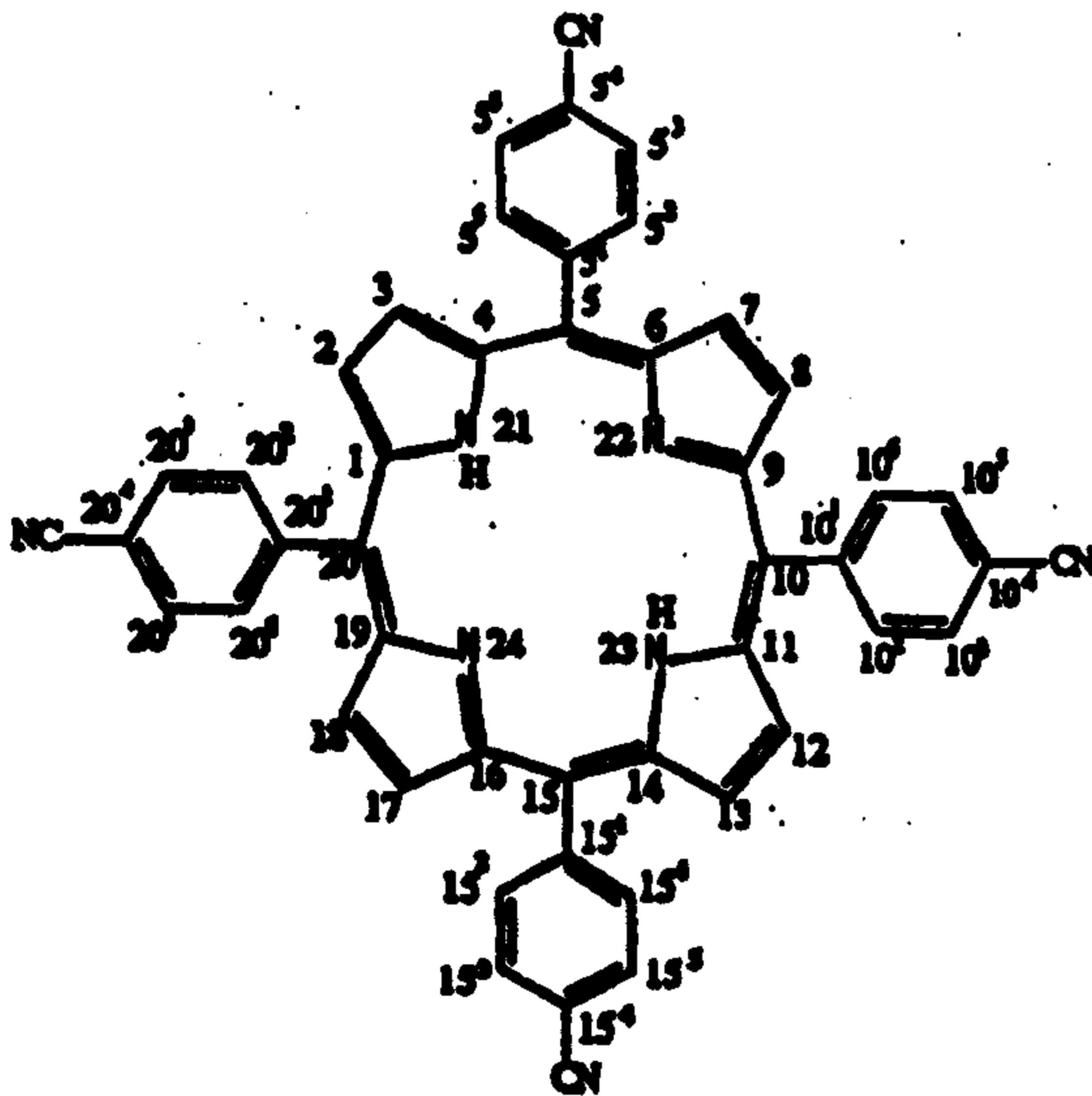
3,7-Diethyl -2,8,12,17- tetramethyl-  
porphyrin



Fischer: Pheoporphyrin a<sub>3</sub>

Systematic Name:

2<sup>1</sup>-Carboxy-7,12-diethyl-2,2<sup>2</sup>-  
dihydro-3,8,13,17-tetramethyl-  
2-oxocyclopentaporphyrin-18-  
propionic acid



Systematic Name:

5',10',15',20' - tetracyano-5,10,15,20-  
tetraphenylporphyrin

Simplified Name:

5,10,15,20-tetra(4-cyanophenyl)porphyrin  
Abbreviated T(4-CN-P)P

Figure 1.4

## 1.3 General Chemistry

### 1.3.1 Tautomerism of the Macrocycle

It has been suggested that the N-H groups in porphyrins exist as different tautomers (Figure 1.5). Early evidence <sup>(4,5)</sup> suggested that the porphyrin favours a 16-membered 18- $\pi$  electron system for the delocalization pathway. However, more recent studies have revealed that the bond lengths indicate a structure in which there are two like-opposite nitrogens. The most stable form of porphyrin, from infrared data and calculations of orbital overlap<sup>(6)</sup>, is that in which the two hydrogens are bonded to opposite nitrogens. A less stable tautomer has been observed<sup>(7)</sup> in which the two hydrogens are bonded to adjacent nitrogens IV (Figure 1.5). This is the less stable tautomer due to the interaction of each hydrogen into the van der Waal's sphere of the other.

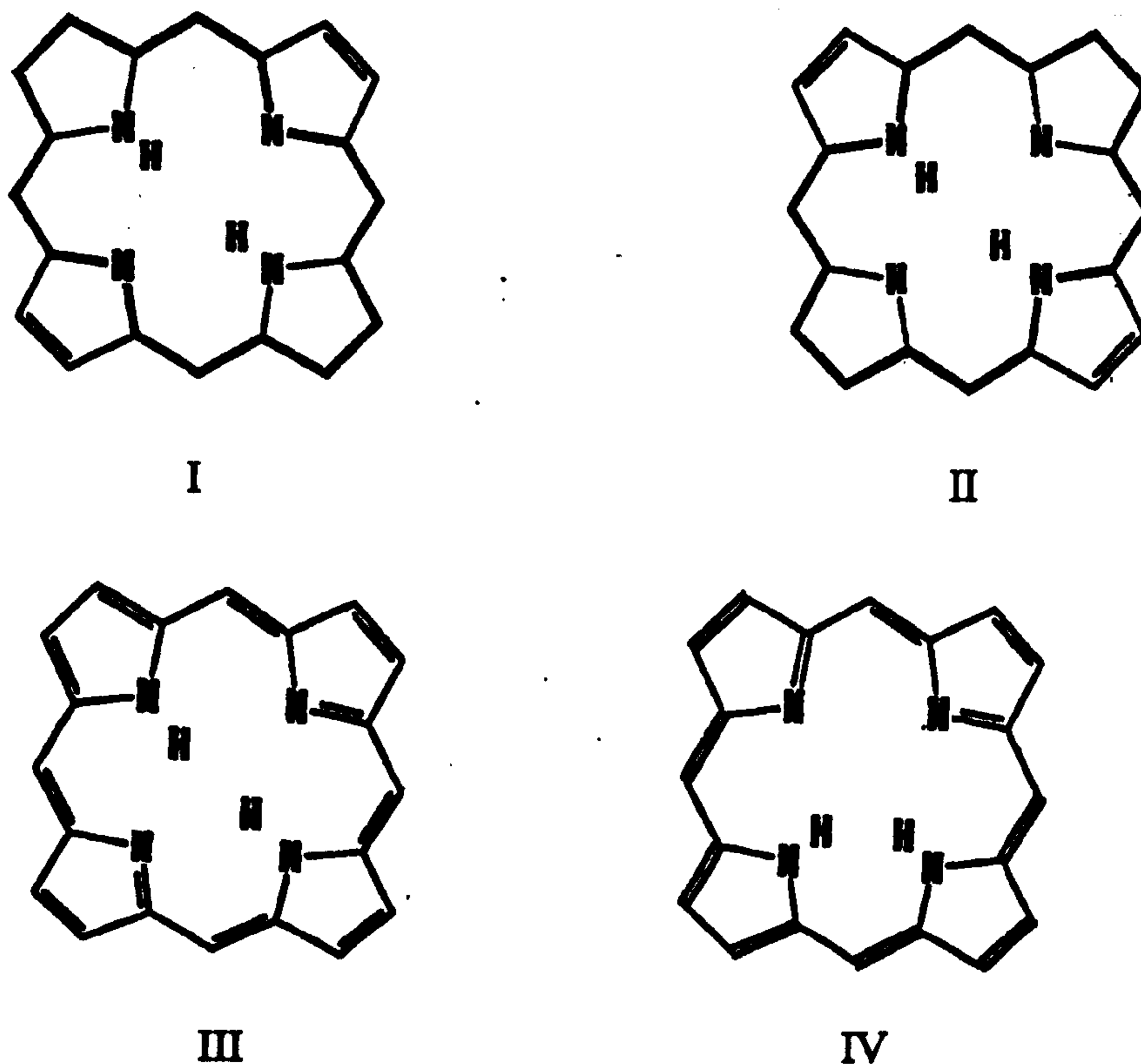


Figure 1.5

### 1.3.2 Aromaticity of the Macrocycle

The porphyrin macrocycle contains a total of  $22\pi$  - electrons, but only  $18\pi$ -electrons are included in any one delocalization pathway. This conforms to Hückels  $4n+2$  rule for aromaticity. The two peripheral double bonds of rings B and D are cross-conjugated and can therefore be reduced while retaining the aromaticity of the molecule. This explains why chlorins (1 bond reduced) and bacteriochlorins (2 reduced bonds) are aromatic compounds. The aromatic character has been confirmed in porphyrin compounds by means of heat of combustion measurements.<sup>(8)</sup> Another requirement of aromatic character is the planarity of the compound and this has been confirmed by x-ray investigations.<sup>(4)</sup>

## 1.4 Synthesis of Porphyrins

Porphyrin systems have been investigated for over 70 years. Since the landmark synthesis by Hans Fischer in 1929, significant progress has been made in the field of porphyrin synthesis.<sup>(9,10)</sup> The synthesis of the porphyrin macrocycle can be approached from a number of directions;<sup>(11)</sup> and for any one method there are three types of pyrrolic precursors : monopyrroles,<sup>(12)</sup> dipyrrolic systems<sup>(13)</sup> and linear tetrapyrroles.<sup>(14)</sup>

### 1.4.1 Co-condensation of a Monopyrrole and an Aldehyde

One of the most difficult porphyrins to synthesise in any great quantity is the parent macrocycle porphin. Fischer and Gleim<sup>(15)</sup> were one of the first to obtain and record the synthesis of porphin, by the condensation of pyrrole and an aldehyde in refluxing methanoic acid. In 1936, Rothmund<sup>(16,17)</sup> also published his synthesis of porphin by heating pyrrole and an aldehyde anaerobically in a sealed tube at  $150^{\circ}\text{C}$  in methanol solution to which a small amount of pyridine was added. This reaction was later extended to include a range of substituted porphyrins using a series of aliphatic and

aromatic aldehydes.<sup>(18,19)</sup> The yields obtained from this reaction were generally less than 3% and almost always contaminated with the corresponding reduced porphyrin, chlorin.

Most of the methods used to synthesise porphyrin also apply in the preparation of  $\beta$ -substituted porphyrins.  $\beta$ -Octasubstituted porphyrins [the simplest being 2,3,7,8,12,13,17,18-octamethylporphyrin ( Figure 1.6 ) in which all  $\beta$ -positions are occupied by methyl groups], were first reported by Fischer and Walach,<sup>(20)</sup> prepared by heating 3,4 - dimethylpyrrole in methanoic acid.

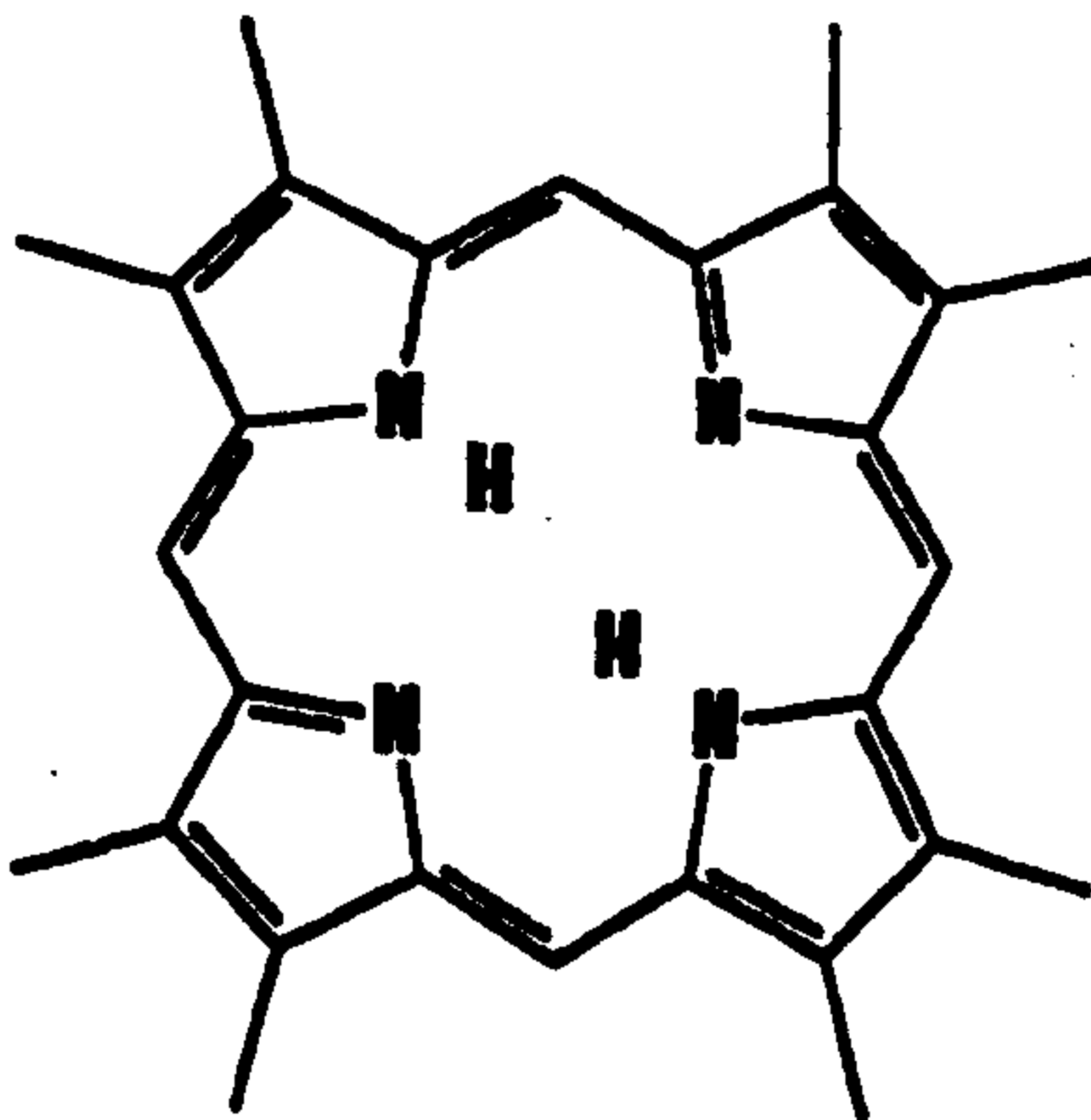


Figure 1.6 Octamethylporphyrin

This method has been extended to obtain several  $\beta$  substituted porphyrins, by simply heating, either dry or in solution, compounds having the general structure 1. (Figure 1.7)

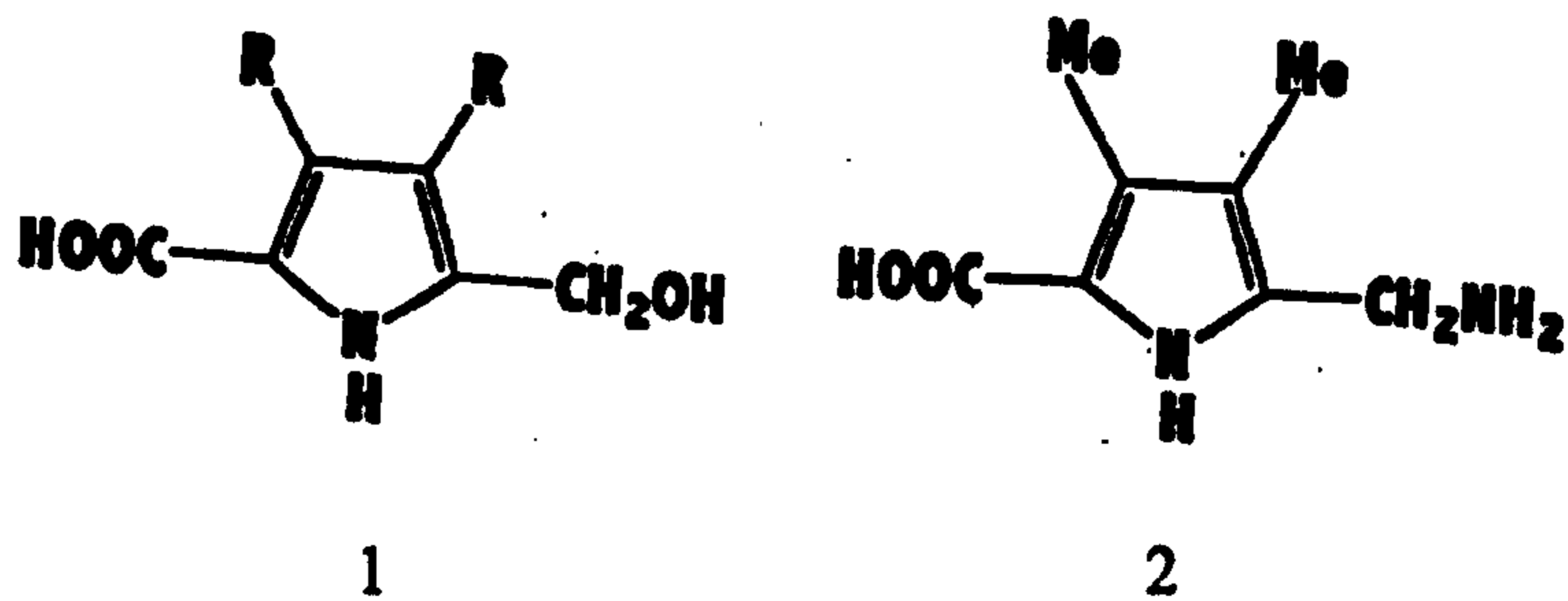


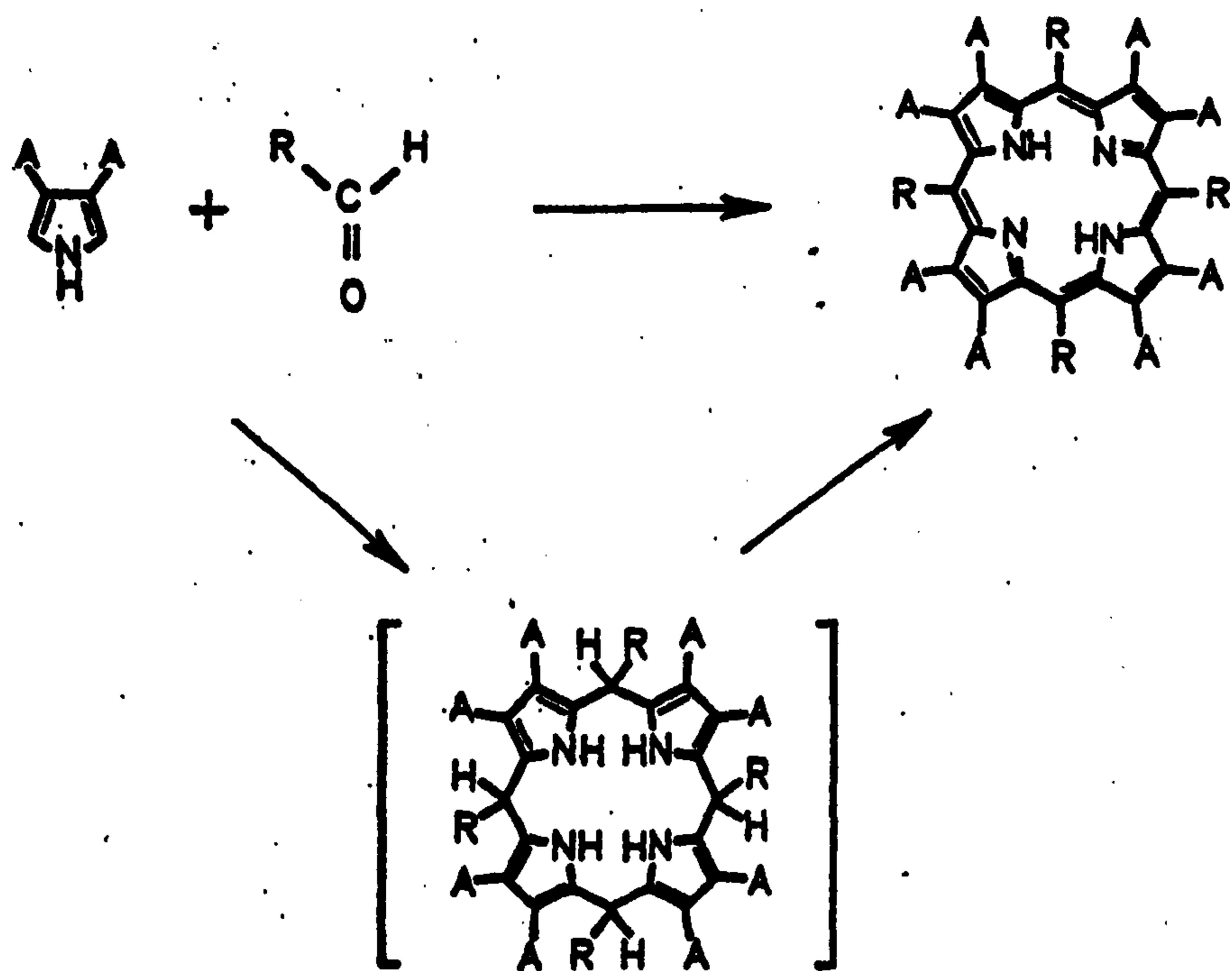
Figure 1.7

The reaction involves a decarboxylation and condensation mechanism, but is only successful when the pyrrolic  $\beta$ -positions are substituted. One of the highest yields (77%) of octamethylporphyrin was obtained from the reaction of 2,3-dimethylpyrrole with formaldehyde in ethanoic acid and pyridine.<sup>(21)</sup> Attempts to synthesise  $\beta$ -octaphenylporphyrin under similar conditions only produced a 26% yield.<sup>(22)</sup> Mannich base reactions have also been utilised in the synthesis of  $\beta$ -octasubstituted porphyrins and yields up to 20% have been achieved by the reaction of 2 with copper (II) acetate in refluxing methanol.

In 1939, Rothmund<sup>(23)</sup> successfully synthesised more than 25 porphyrins by the condensation of aliphatic, aromatic and heterocyclic aldehydes with pyrrole. This method, which produces meso-tetrasubstituted porphyrins, has its limitations due to the symmetric nature of the porphyrin produced.

Adler, Longo and co-workers<sup>(24,25)</sup> showed an improvement in the yields of the porphyrins by simply carrying out the reactions in acidic media open to the air. Yields of approximately 20% of tetraphenylporphyrin were obtained from the reaction of equivalent amounts of benzaldehyde and pyrrole in refluxing propionic acid.<sup>(25)</sup> Yields of 38-40% can be obtained by using ethanoic acid, but the purification and isolation is made difficult due to the higher  $pK_a$  value of ethanoic acid.

More recently Lindsey et al<sup>(26)</sup> developed a more general synthetic method for meso-tetraphenylporphyrins. (Scheme 1)



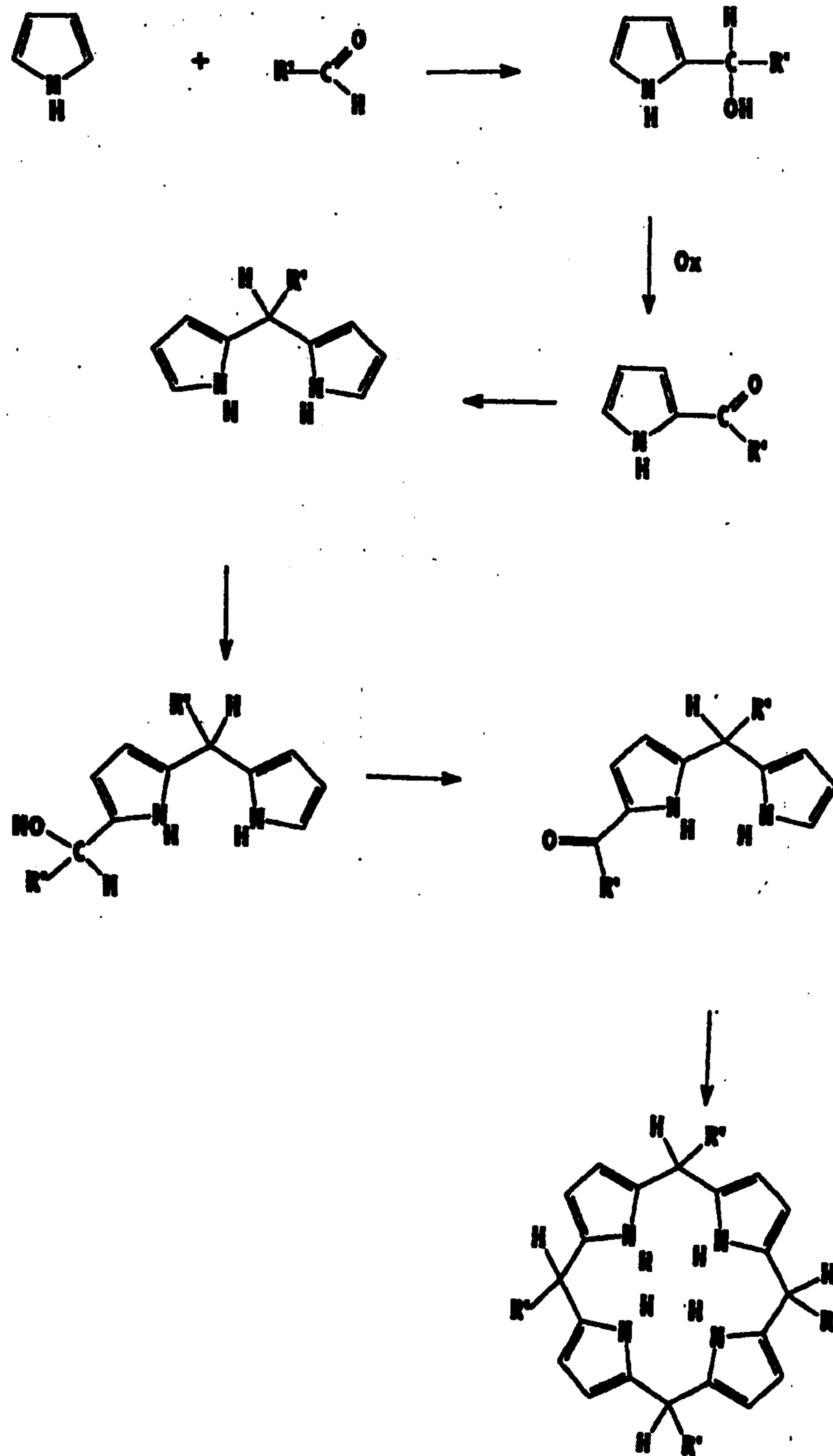
[3]

Scheme 1

This takes into account that under equilibrium conditions, the acid catalysed condensation proceeds via the porphyrinogen 3. Dolphin,<sup>(27)</sup> who was able to isolate a porphyrinogen, showed that treating the intermediate with an oxidising agent produced the porphyrin. The Lindsey modification is a two-step one pot procedure to form the porphyrinogen by acid catalysis under anaerobic conditions and then oxidising to the porphyrin by addition of an oxidant.

In order to understand the formation of the porphyrin under these conditions, a detailed mechanistic scheme must be considered (Scheme 2). Early workers,<sup>(28)</sup> proposed a scheme in which the Rothmund reaction of pyrrole and benzaldehyde formed a carbinol. Oxidation to a ketone followed by a second condensation, dehydration and reduction led to a dipyrromethane. The dipyrromethane then reacts with another molecule of aldehyde to form another carbinol, which again is oxidised to a ketone. Condensation of two molecules,

followed by a loss of water produces the porphyrinogen, which can produce either chlorin or porphyrin.



Scheme 2

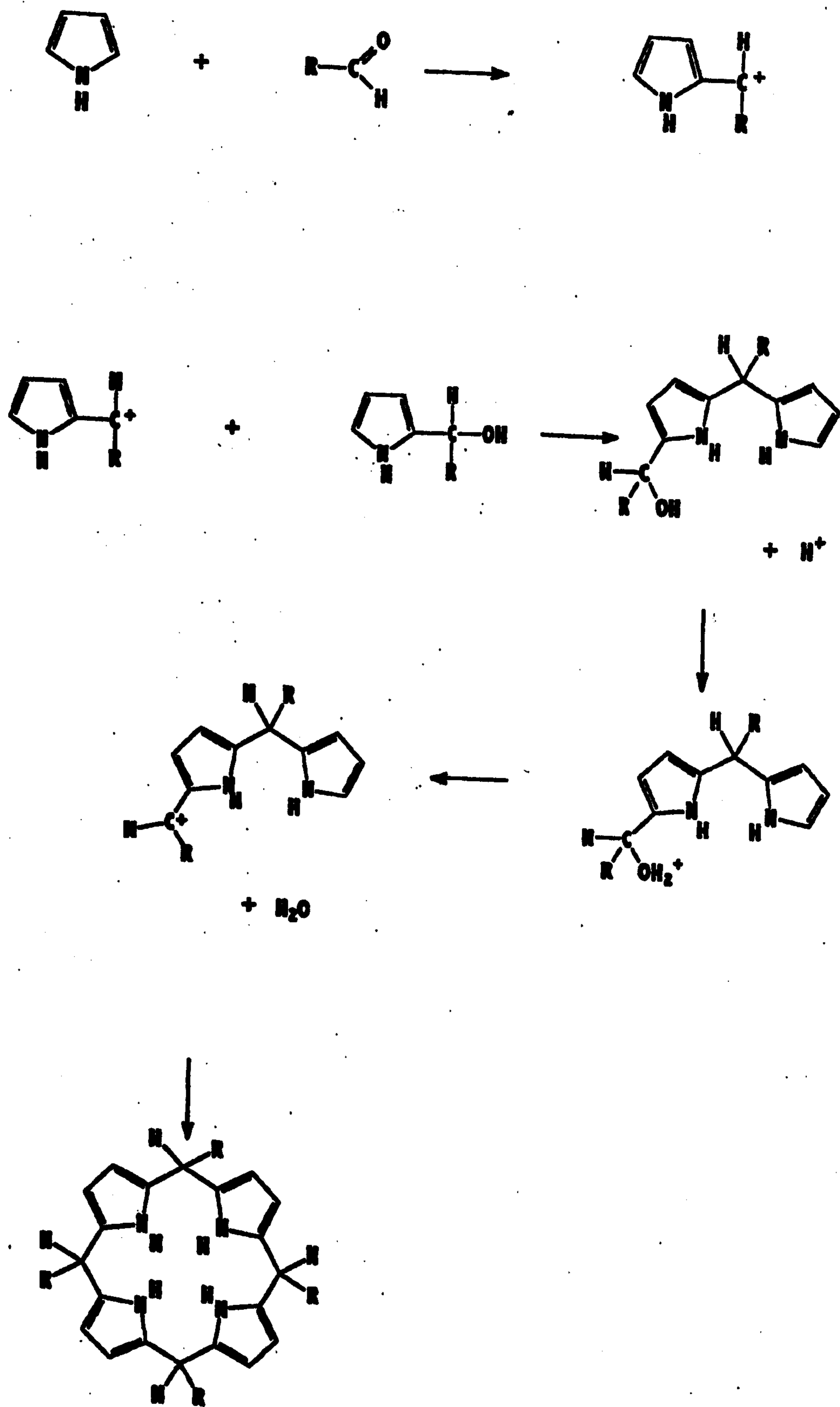
Later studies by Adler et al,<sup>(29)</sup> on the aerobic condensation of pyrrole and benzaldehyde ruled out the mechanistic scheme suggested by Badger et al.<sup>(28)</sup>

In addition to the rapid appearance of water it was also observed that:

- (1) an oxidant was required for the formation of the porphyrin;
- (2) a species is formed early in the reaction which has an absorption maximum near 480 nm, but disappears on porphyrin formation;
- (3) the product is always contaminated with a small percentage of chlorin.

The scheme proposed suggests that the carbonium ion is formed on the condensation of pyrrole and an aldehyde, with the subsequent loss of water. This carbonium ion then attacks the free  $\alpha$ -position of another pyrrole; the functional group on the second pyrrole continues the condensation. Chain building continues producing tetrapyrrolylcarbinols, which can undergo cyclisation to form the porphyrinogen, which followed by subsequent oxidation gives the porphyrin (Scheme 3).





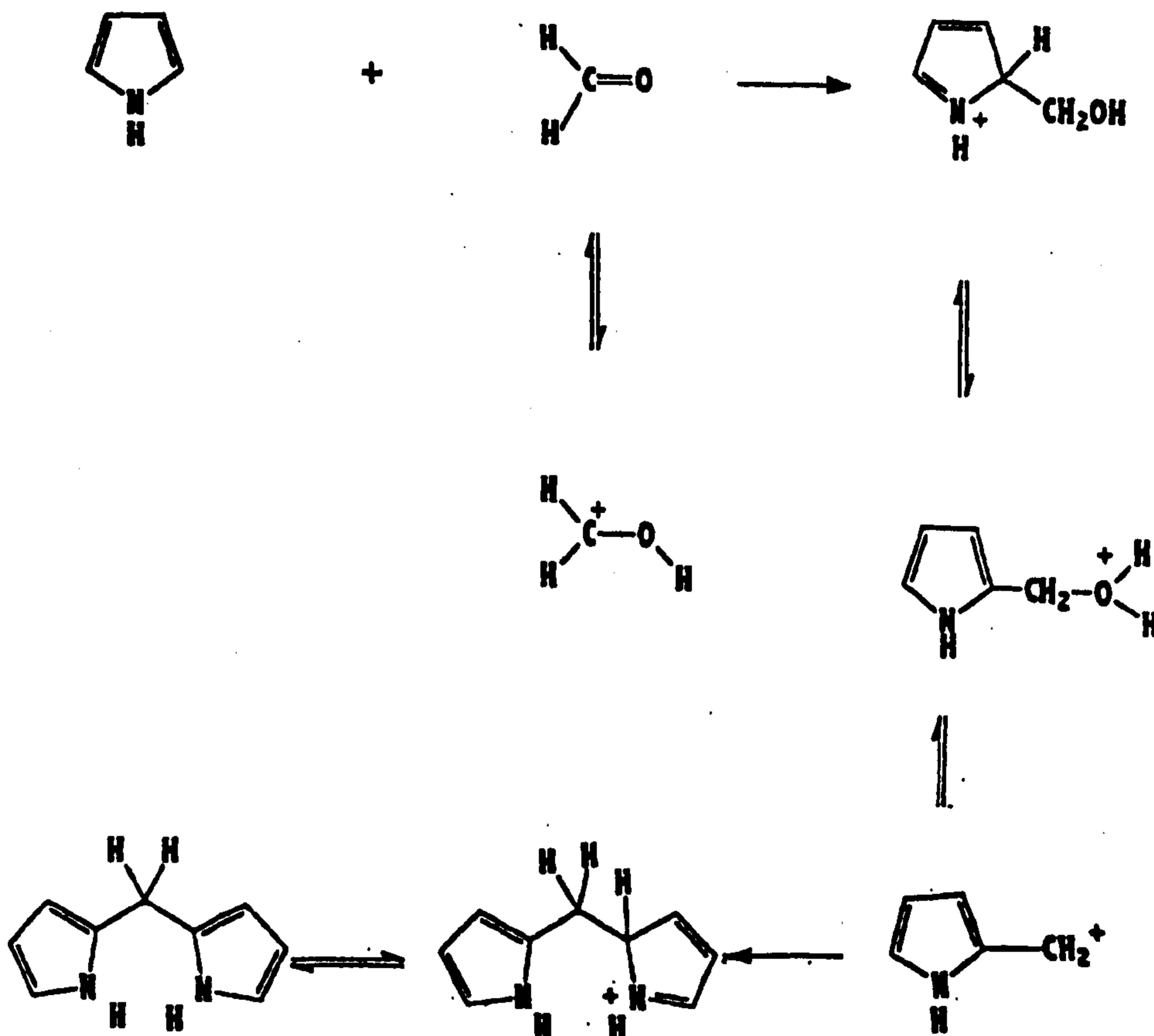
Scheme 3

## 1.4.2 Direct Coupling of Dipyrrolic Intermediates

This method has been used extensively in porphyrin synthesis due to the variety of unsymmetric  $\beta$ -substitution patterns that can be achieved. Also known as the "2+2 synthesis", dipyrromethanes and dipyrromethenes are the most widely used intermediates carrying suitable functional groups at the  $\alpha$ -positions in order to couple to each other. These are synthesised from monopyrroles which are obtained from the classical Knorr reactions.<sup>(30)</sup>

### Dipyrromethanes

Dipyrromethanes can be regarded as the result of the condensation of two pyrrole units with an aldehyde (Scheme 4). For meso-unsubstituted porphyrins, formaldehyde is employed, but a series of substituted porphyrins can be synthesised by using substituted aliphatic and aromatic aldehydes.<sup>(31)</sup>



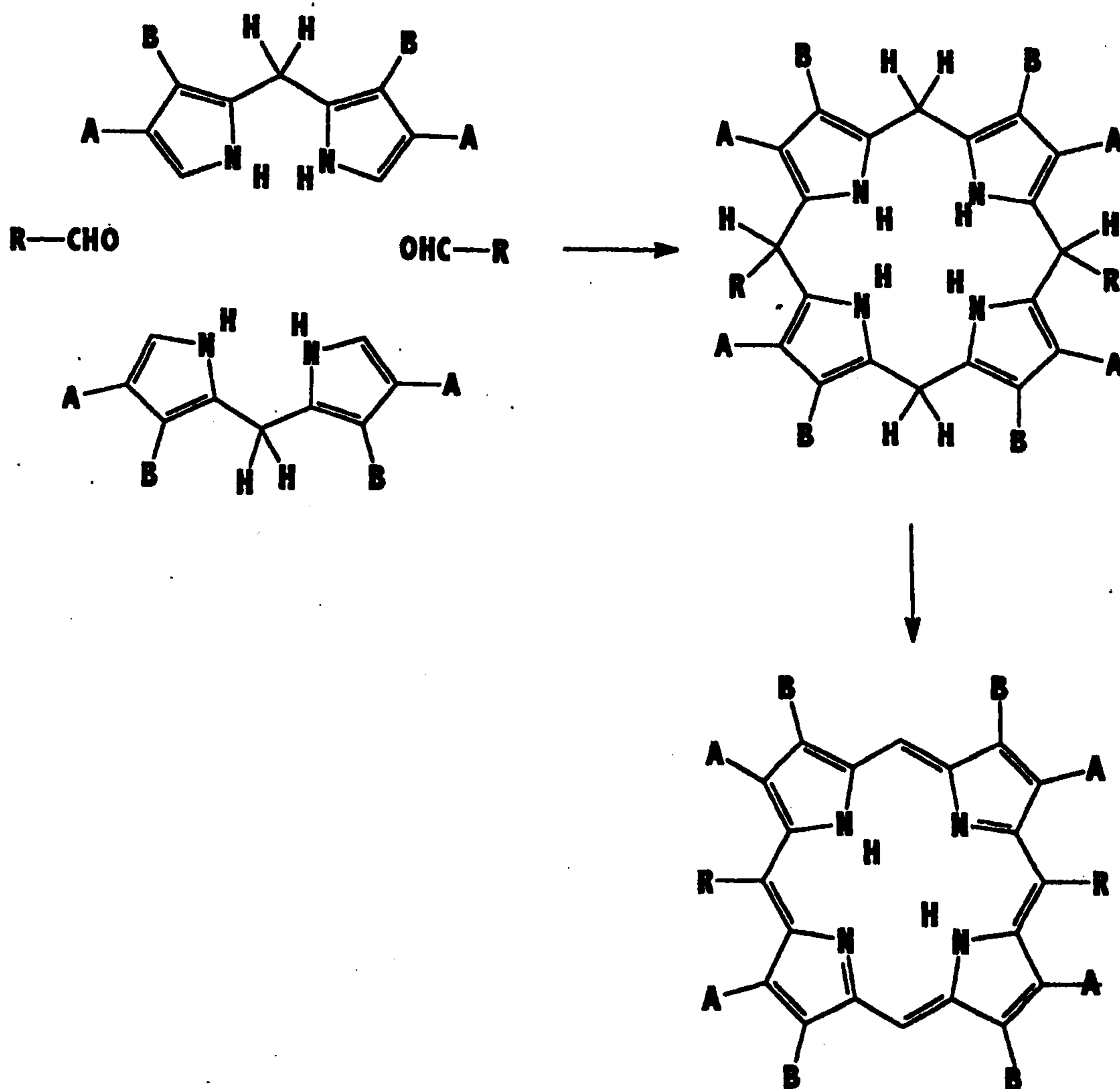
Scheme 4

MacDonald<sup>(32)</sup> was the first to introduce a synthesis involving dipyrromethanes, which was later modified by Kenner.<sup>(33)</sup> The MacDonald reaction involved the acid catalysed condensation of 5,5-diformyldipyrromethanes with 5,5-unsubstituted dipyrromethanes to yield an intermediate that is rapidly oxidised to the porphyrin in air.

Ogoshi et al<sup>(34)</sup> have reported the synthesis of 5,15-diarylporphyrins by the co-condensation of 5,5-unsubstituted dipyrromethanes and aromatic aldehydes. By carrying out the reactions in refluxing propionic acid/zinc acetate, several meso-substituted porphyrins have been isolated in 15-25% yields.

Gunter and Maunder<sup>(31)</sup> showed that this acid catalysed reaction proceeded via a porphyrinogen intermediate as previously encountered for the condensation of pyrrole and benzaldehydes.

In attempts to increase the yields and stability of sensitive substituents, several modifications have been reported. Lawrence et al<sup>(35)</sup> reported the synthesis in which he employed the condensation of an unsubstituted dipyrromethane and substituted benzaldehydes in dichloromethane at room temperature in the presence of catalytic amounts of trifluoroacetic acid, with the porphyrinogen being oxidised with a p-chloranil (Scheme 5).

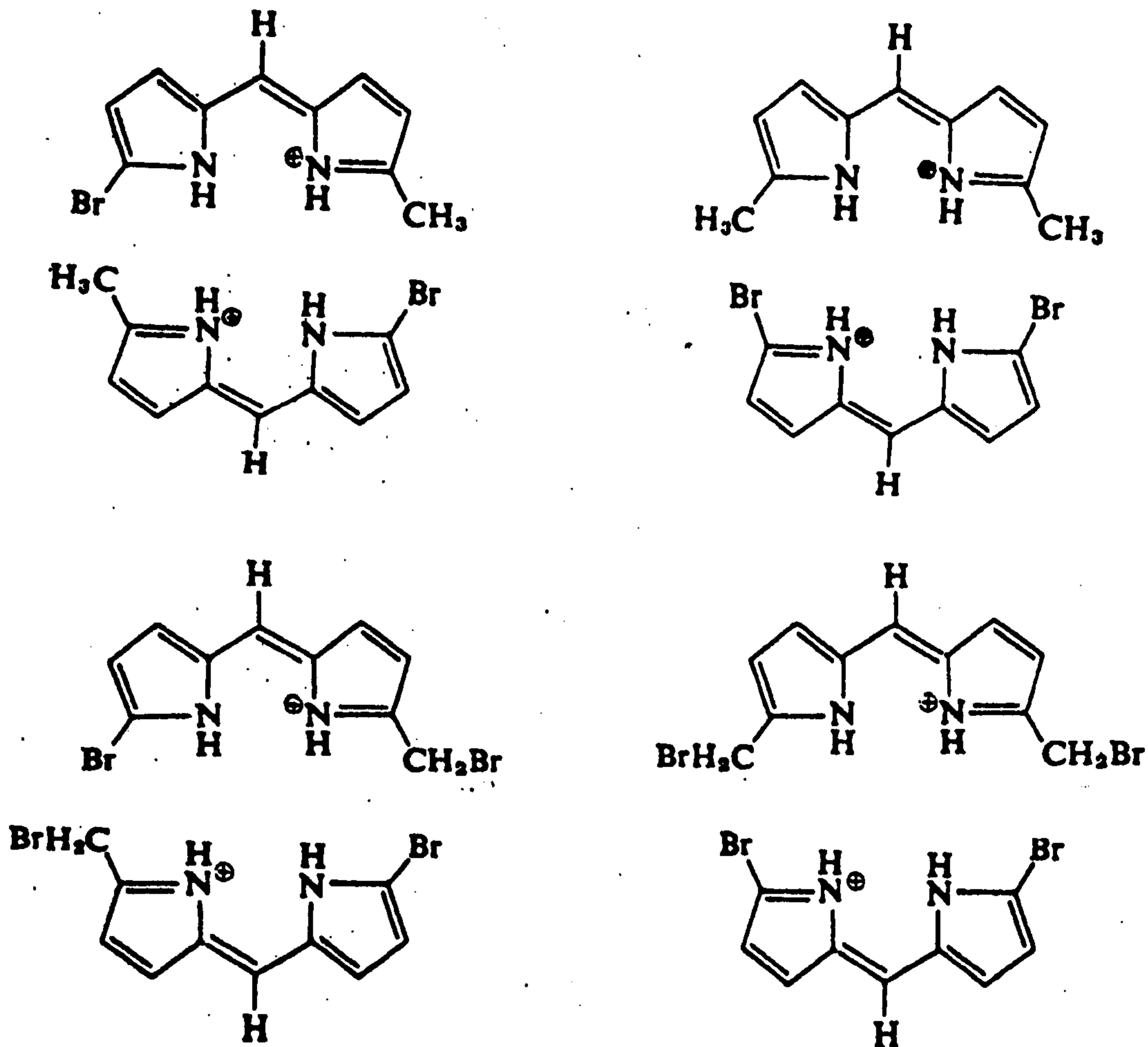


Scheme 5

### Dipyrromethenes

Dipyrromethenes are formed by a two-electron oxidation of dipyrromethane, but differ considerably in stability and reactivity from the dipyrromethanes. Dipyrromethenes formed the backbone of Fischer's classical porphyrin synthesis <sup>(37)</sup> largely because of the harsh reaction conditions encountered.

The coupling reaction involved the fusion in succinic acid, of one of the four pairs of dipyrromethene intermediates (Scheme 6) for several hours exposed to air.



Scheme 6

The yields were generally low since the harsh reaction conditions adversely affected the sensitive  $\beta$ -substituents. The dipyrromethenes are activated towards self condensation and have been used in porphyrin synthesis with milder reaction conditions. <sup>(37)</sup>

The Fischer approach is only applicable to prepare porphyrins with  $C_{2h}$  symmetry using the readily available 5'-carboxy-5-methyl-dipyrromethenes.

Recent studies<sup>(38)</sup> have shown that refluxing 5,5'-dibromodipyrromethene and 5,5'-dimethyldipyrromethene in anhydrous methanoic acid with one equivalent of bromine yields 20-40% porphyrin.

### 1.4.3 Cyclization of Linear Tetrapyrroles

The need to synthesise porphyrins with totally unsymmetric  $\beta$ -substitution led to the direct development of procedures involving the coupling of individual pyrroles to give a linear tetrapyrrole, which is cyclized in the final step to give the porphyrins. Bilenes b, biladienes ac; a-oxobilanes and b-oxobilanes are the most commonly used precursors.<sup>(39)</sup>

The nomenclature is based on that of the bile pigments, and the numbering fits in with the IUPAC recommendations for the nomenclature of porphyrins<sup>(2)</sup> (Figure 1.8).

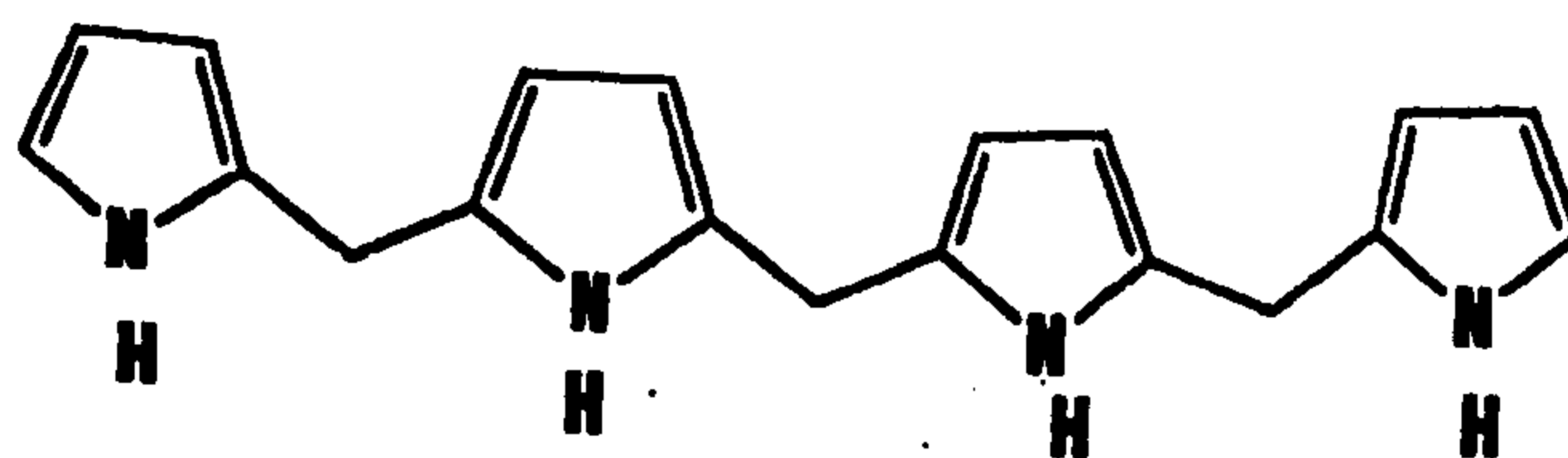
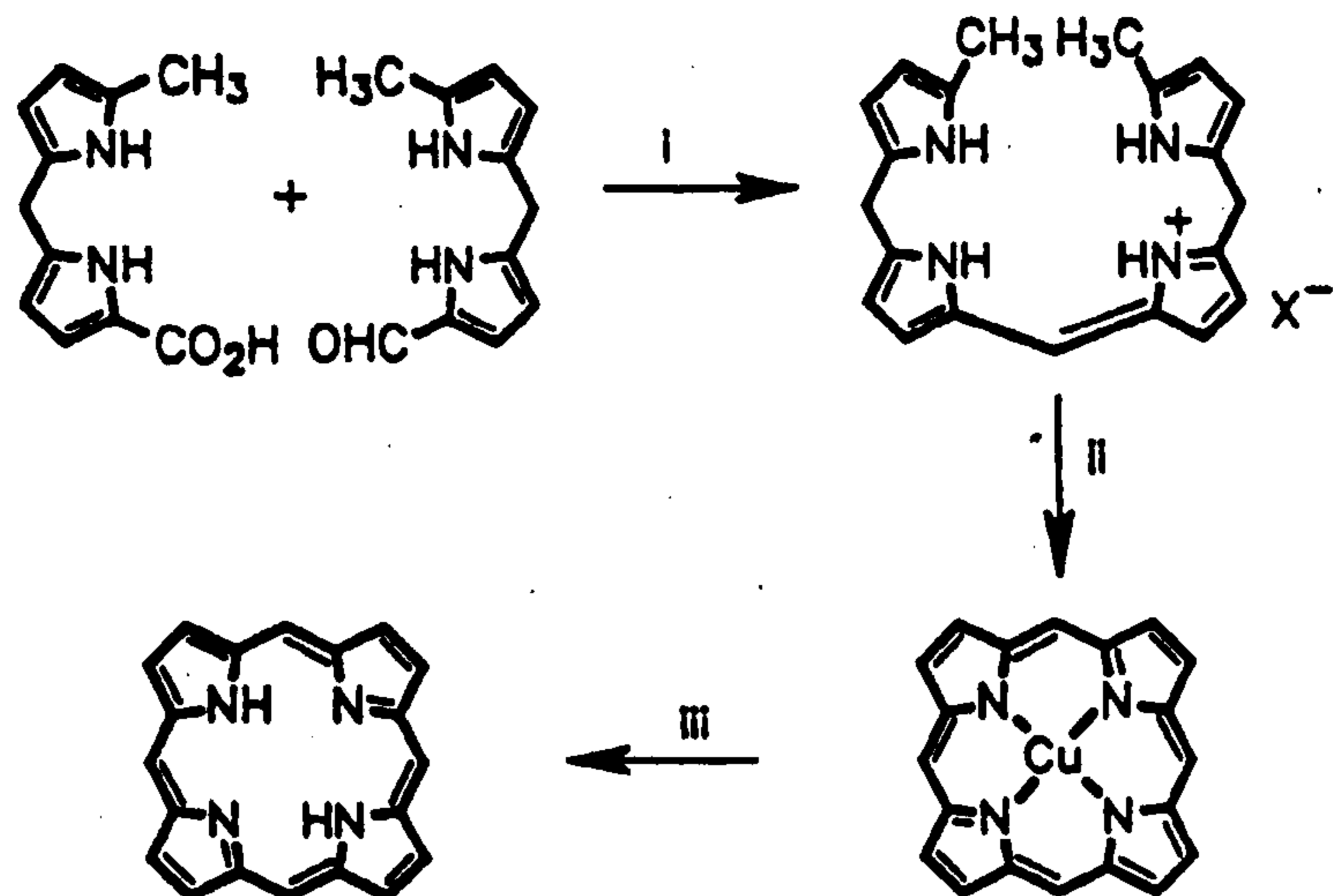


Figure 1.8 Bilane.

The methylene links between the pyrrole rings are very sensitive to oxidation and attack by electrophilic species.

#### **Porphyrins from bilenes b**

Bilenes b, are prepared by the acid catalysed coupling of 5-carboxydipyrromethane with a 5-formyldipyrromethane (Scheme 7). The most commonly used method to make the porphyrin from the bilene b, is the cyclisation to the copper complex of the porphyrin using copper (II) salts. The free base porphyrin is achieved by the removal of copper with strong acids.

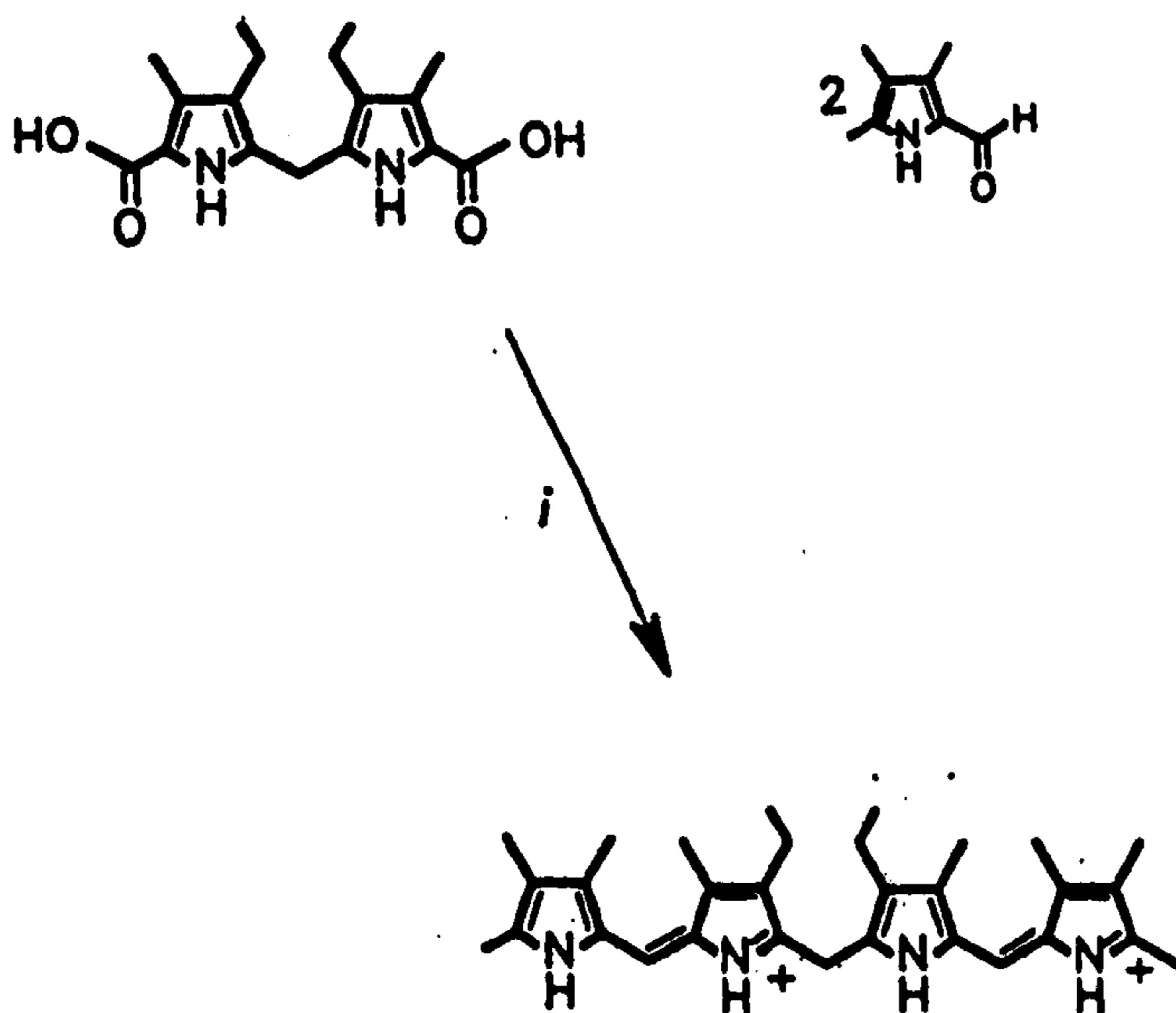


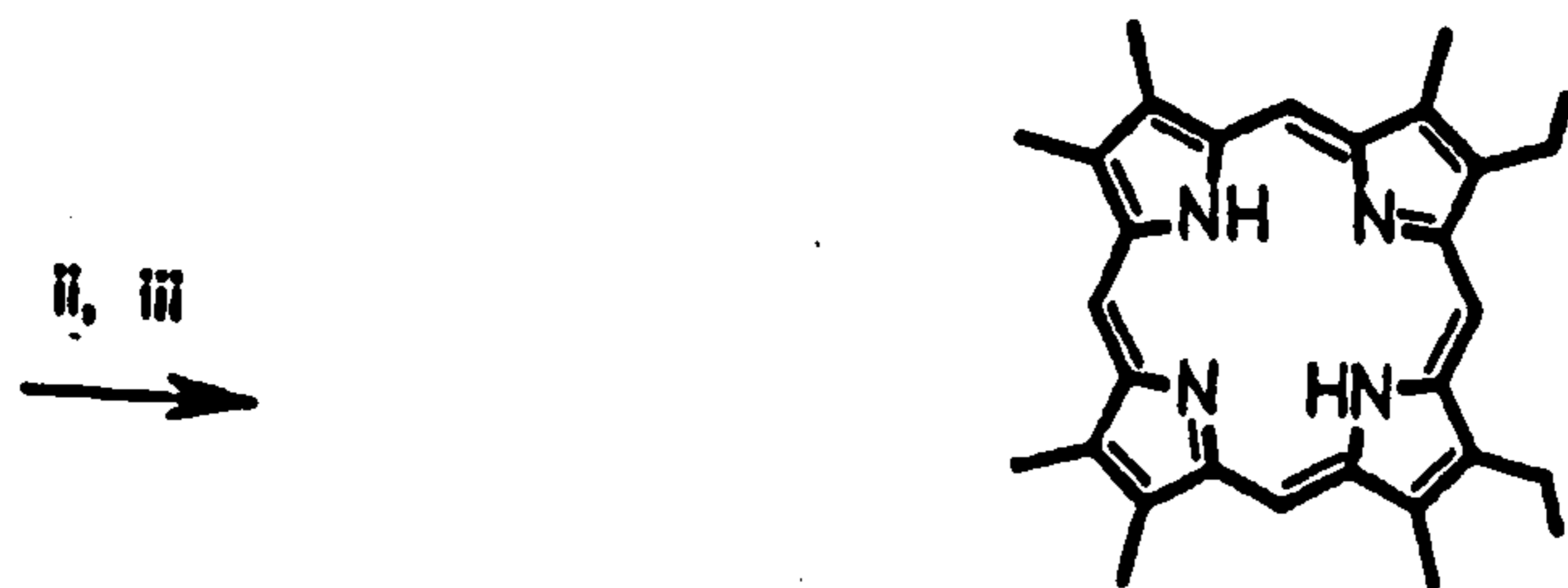
- i)  $\text{CF}_3\text{CO}_2\text{H}$ , then  $\text{CH}_3\text{OH}$  and  $\text{HBr}$   
 ii)  $\text{Cu}(\text{OAc})_2$  in  $\text{CH}_3\text{CO}_2\text{H}/\text{CH}_3\text{OH}$ ,  $100^\circ\text{C}$ ;  
 iii)  $\text{H}_2\text{SO}_4/\text{CF}_3\text{CO}_2\text{H}$

Scheme 7

### Porphyrins from Biladienes -ac

Biladienes-ac are commonly prepared and handled in their protonated form, usually as the crystalline dihydrobromides. Biladienes are the most commonly used linear tetrapyrroles in porphyrin synthesis. Johnson and Kay<sup>(40)</sup> were the first to prepare biladienes-ac by the acid-catalysed condensation of 2-formyl-5-methylpyrrole with a dipyrromethane-5,5'-dicarboxylic acid (Scheme 8) to give 20-30% yield.

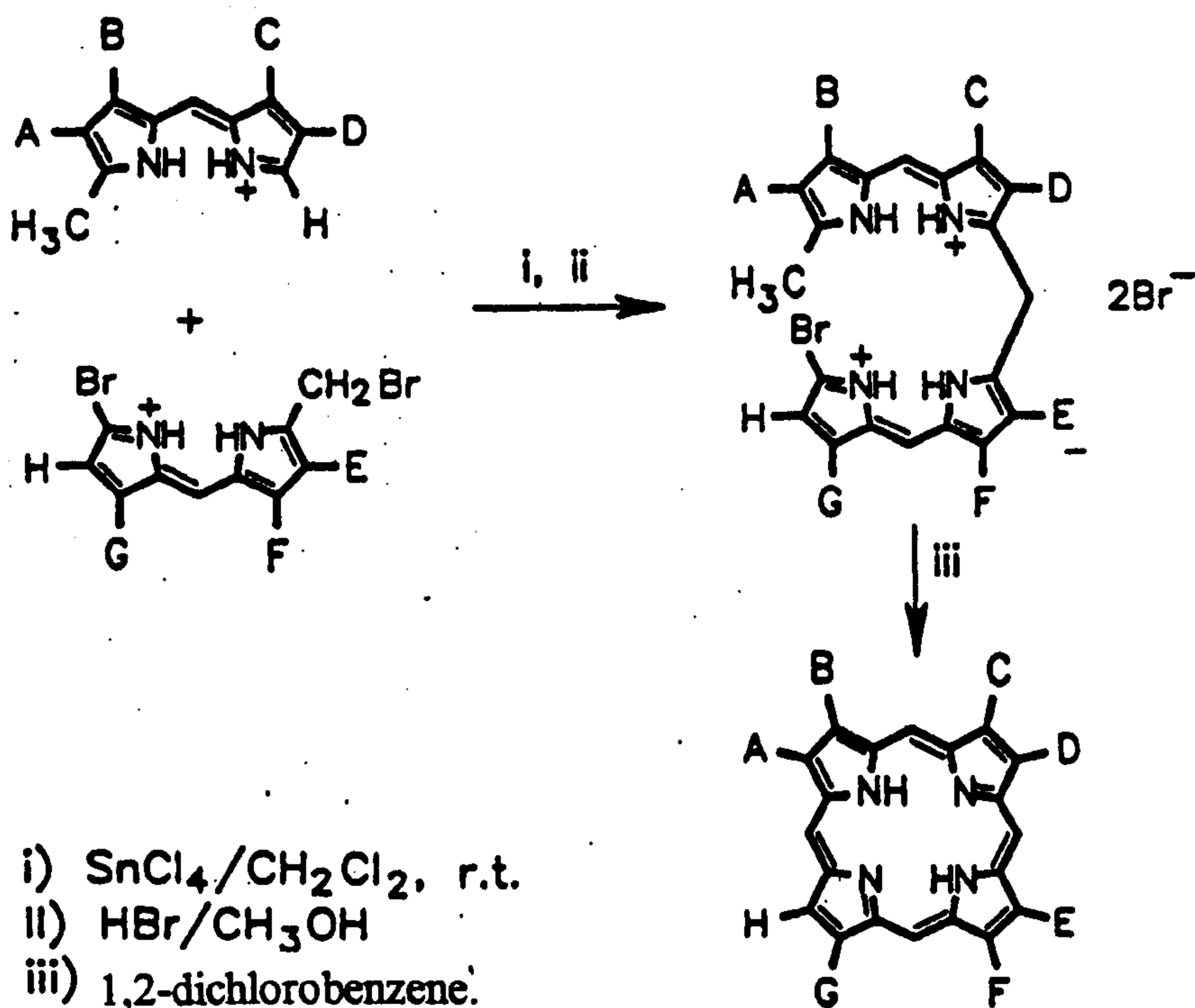




- i) HCl in CH<sub>3</sub>OH, r.t.;
- ii) Cu(OAc)<sub>2</sub> in CH<sub>3</sub>OH, reflux 48 h;
- iii) H<sub>2</sub>SO<sub>4</sub>

Scheme 8

Johnson and co-workers<sup>(41)</sup> developed a regioselective synthesis of octa-alkyl porphyrins using 1-bromo-19-methylbiladienes as the tetrapyrrolic precursors (Scheme 9). The biladiene is prepared from dipyrromethenes rather than dipyrromethanes in the presence of tin (IV) chloride to give the tin complex of the biladiene. Treatment with methanolic hydrobromic acid gives the required biladiene salt which is cyclized to the porphyrin by refluxing in 1,2-dichlorobenzene<sup>(41)</sup>.



Scheme 9

This two-step procedure has been used to synthesise several porphyrins in high yield: the range including unsymmetric porphyrins,<sup>(42)</sup> singly and doubly linked



porphyrin dimers,<sup>(43,44)</sup>  $\beta$ -unsubstituted<sup>(45)</sup> mono- and divinyl porphyrins<sup>(45,46)</sup> and uroporphyrins I and III.

## 1.5 Metallation of Porphyrins

A porphyrin derivative in which at least one of the central nitrogen atoms forms a bond with a metal atom is called a metalloporphyrin. The formation of a metalloporphyrin usually involves the reaction between the porphyrin free base [ $H_2(P)$ ] with a metal salt ( $MX_2$ ). During the metallation of a porphyrin there are essentially five steps that have to be followed. They are as follows:

### (a) Protonation-deprotonation equilibrium



At some stage, deprotonation has to occur in order to produce the  $P^{2-}$  ion which coordinates to the metal ion. Therefore, the presence of strong acids impedes or even reverses metallation but the presence of reagents that absorb protons will enhance and favour the process.

### (b) Release of metal ion from the metal carrier

In order to provide an active species, the metal compound which carries the metal ion dissociates in the reaction medium producing a coordinately unsaturated species which combines within the  $P^{2-}$  dianion. The choice of carrier depends on activity, availability and solubility in solvent.

**(c) Formation of  $MN_4$  System**

The four central pyrrolic nitrogens of the porphyrin co-ordinate to the unsaturated metal ion. The divalent metal ions (Ni, Cu) which prefer square planar arrangements, produce stable metalloporphyrin complexes.

**(d) Charge neutralisation**

For metal ions with a charge greater than +2, a charge neutralisation is required. This needs to be neutralized to attain electroneutrality and is achieved by axial co-ordination with anionic ligands.

**(e) Completion of co-ordination sphere**

This occurs when a metal ion prefers to exist in an octahedral environment. The co-ordination sphere is completed by further complexation with neutral donor ligands (water, pyridine).

There are several metallating systems available and therefore care should be taken in choosing the appropriate system. The previous five steps, along with solvent system, metal carrier, activity etc. should be taken into account to ensure the optimum reaction conditions are achieved. There are nine various solvent combinations for different metallations. The following methods describe those used in this study.

## 1. Chloroform/Methanol Method

A refluxing solution of chloroform containing the porphyrin is treated with a saturated solution of the metal acetate in methanol. The reaction is followed by absorption spectroscopy and on completion the mixture is concentrated and diluted with methanol allowing crystallisation of the product, while the excess metal carrier remains in solution. This method has been employed to introduce divalent metal ions including Zn(II), Co(II) and Ni(II)<sup>(47)</sup> porphyrins.

## 2. Dimethylformamide Method <sup>(50)</sup>

Adler and co-workers<sup>(48)</sup> have successfully inserted metals into over 60 porphyrins by refluxing a metal salt (usually metal chlorides) in weakly co-ordinating, high boiling oxygen-donor solvents such as dimethylformamide. DMF is a good solvent for both porphyrins and the metal salts. Best results are obtained using anhydrous metal chlorides with the product crystallizing out on direct dilution with water or with dilute HCl to dissolve the excess metal salt left in the reaction mixture.

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## 2 Characterisation of porphyrin macrocycles .

### 2.1 The Electronic Absorption Spectra of Porphyrins

Porphyrins, being highly coloured compounds exhibit characteristic absorption properties in the uv-visible region. For a metal free porphyrin, the spectrum consists of an intense absorption in the region 400-430 nm. This is referred to as the Soret or B band and normally has an extinction coefficient in the region  $\epsilon \approx 10^5$ . In addition, these systems exhibit four weaker, less intense bands in the region 450-700 nm. These bands are designated IV, III, II, I and the relative intensities are determined by the nature and position of the porphyrin's peripheral side chains.<sup>(1)</sup>

Four general classifications of spectra have been observed based on the relative intensities of the four visible bands. Gouterman<sup>(1)</sup> has proposed an interpretation of the spectral differences based on the perturbations of the  $\pi$ -electron levels by the electronic nature of the porphyrin's side chains (Figure 2.1).

#### 1 ETIO (IV > III > II > I)

Characteristic of a porphyrin system in which 6 or more of the  $\beta$ -pyrrolic positions are substituted with alkyl chains, with the remaining two being unsubstituted. examples of which include proto- and deuteroporphyrin IX.

#### 2 Rhodo (III > IV > II > I)

Characteristic of a porphyrin system in which one strongly electron-withdrawing group (e.g. acetyl, carboxyl) is attached to the conjugated system. This produces an intensifying effect to band III and a bathochromic shift (red shift) to all the bands.

3. **Oxorhodo (III>II>IV>I)**

Characteristic of porphyrins in which two electron-withdrawing groups are situated diagonally on opposite pyrrole rings. This in effect is enhancing the rhodofying effect.

4. **Phyllo (IV>II>III>I)**

Characteristic of porphyrins in which (a) single meso-alkyl substitution and (b) when four or more of the  $\beta$ -positions are unsubstituted.

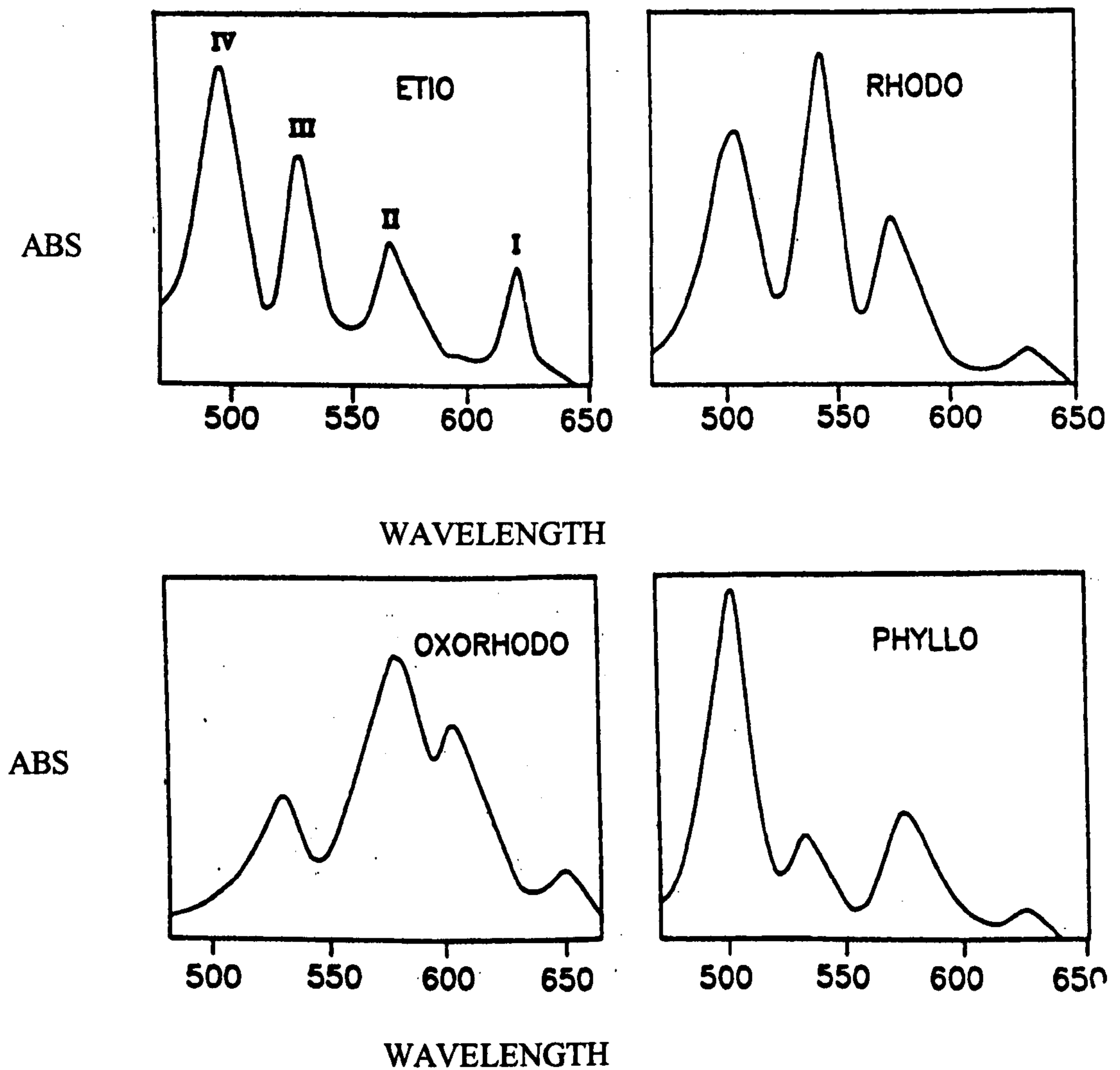


Figure 2.1



At low pH, the inner nitrogens of porphyrins can be protonated (accepting two additional protons) to form dicationic species.<sup>(2)</sup> Formation of the di-cation produces a visible spectrum that differs considerably to the corresponding free base. As shown in Figure 2.2, protonation results in a large bathochromic shift of the B+Q bands, with the visible bands also collapsing essentially to two bands. Under these circumstances, there is an increase in symmetry as the  $D_{2h}$  symmetry for the free base approaches a  $D_{4h}$  symmetry. The change in the visible spectrum is accompanied by a colour change of the meso-tetraarylporphyrins, from a deep red to an emerald green. For meso-unsubstituted porphyrins the bathochromic shifts and the Q band intensities are markedly less and this is represented with a mild colour change from red to magenta.

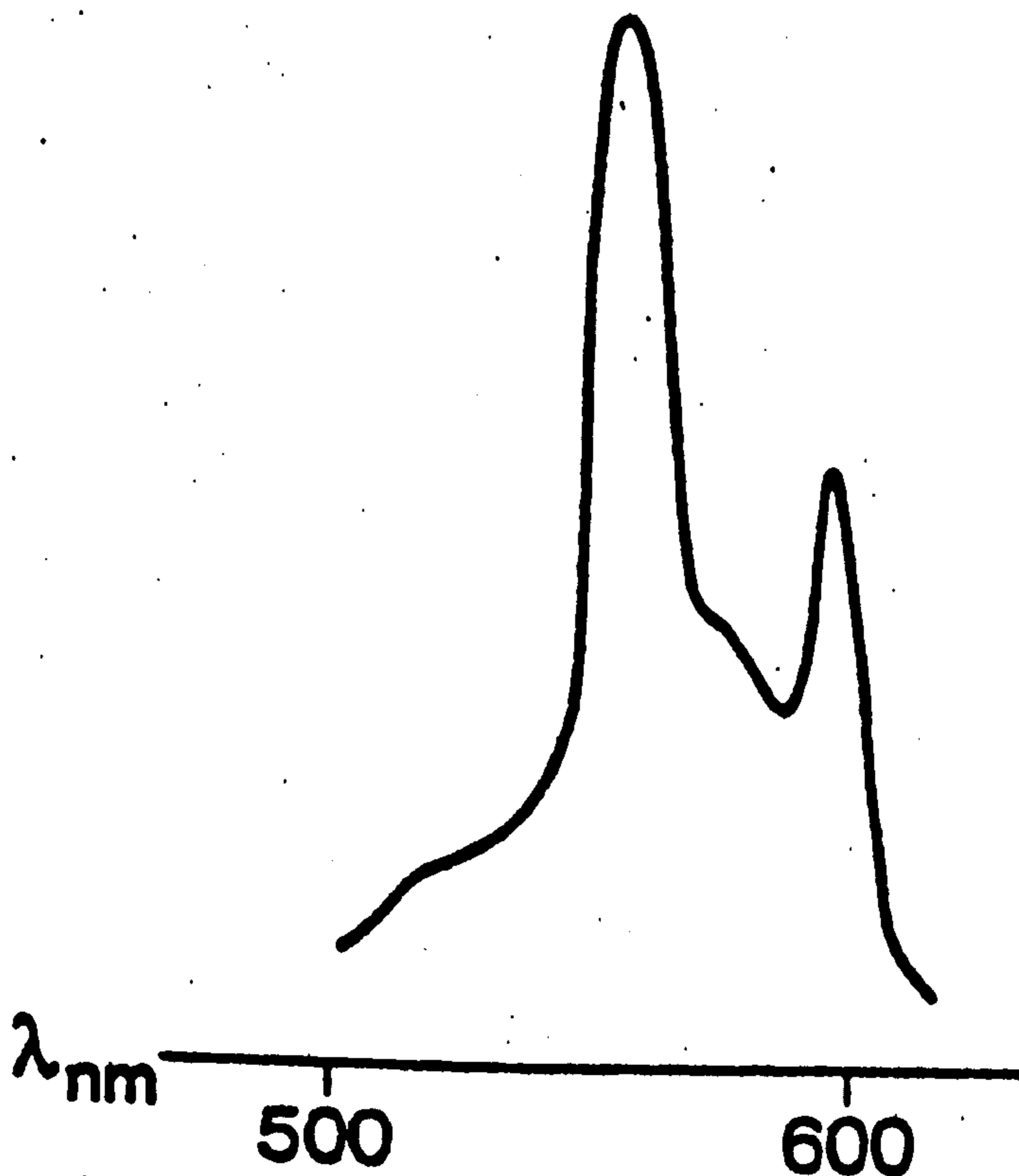


Figure 2.2

The optical spectra of the porphyrin macrocycle can be significantly altered by alterations to the conjugation pathway. This is achieved by the reduction of one or two of the peripheral double bonds producing chlorins and bacteriochlorins respectively. Although the aromaticity of the macrocycle is still present, the optical spectrum is altered considerably as shown in Figure 3.3. For the reduction of one double bond, a strong absorption at  $\lambda = 650 - 680$  nm is obtained and reduction of both  $\Delta^7$  and  $\Delta^{17}$  double bonds produces an intense absorption at  $\lambda = 740$  nm.

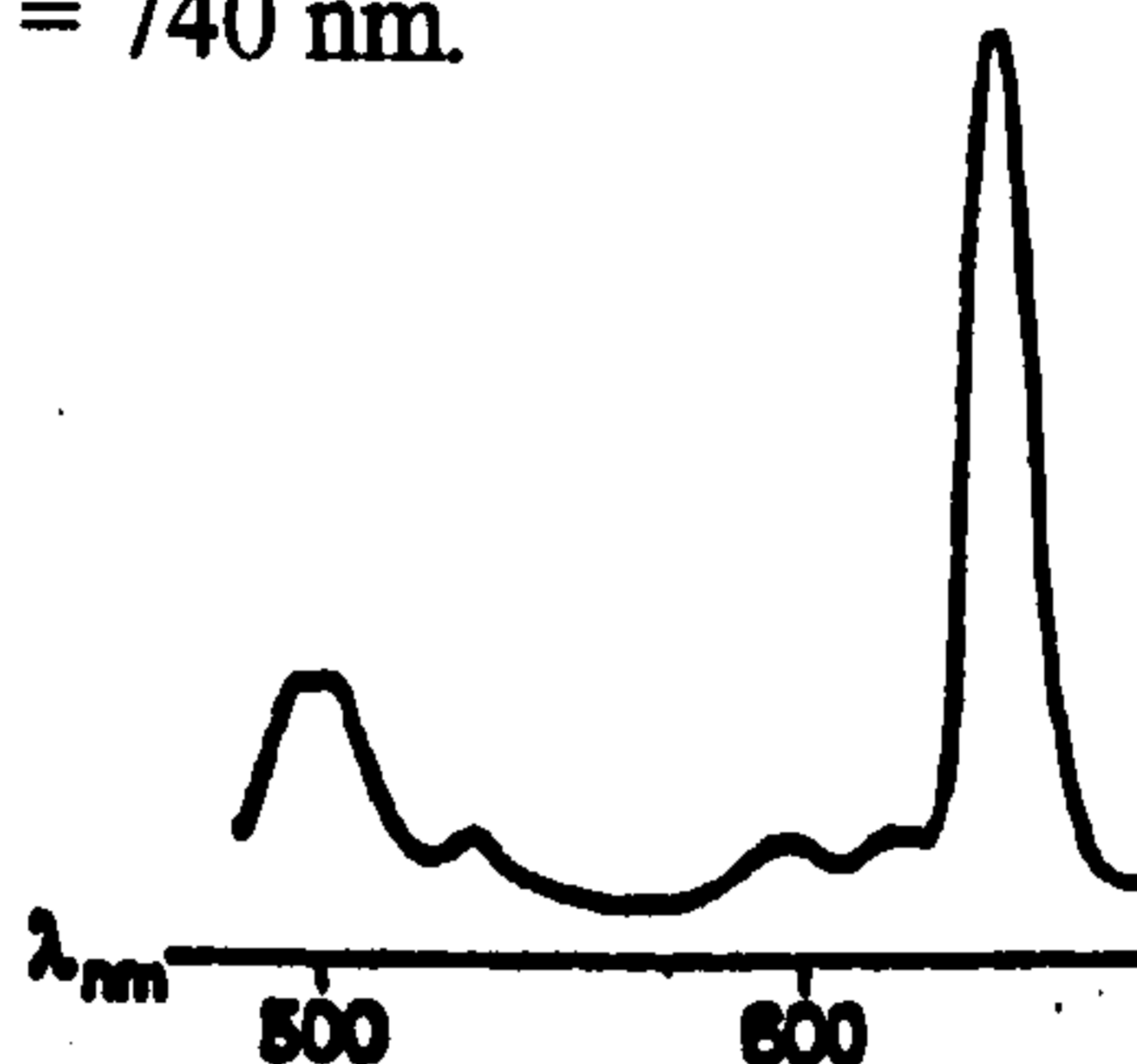


Figure 3.3 Chlorin uv spectrum

## 2.2 The Electronic Absorption Spectra of Metalloporphyrins

Metallation of the porphyrin macrocycle effects the optical absorption properties of the porphyrins.<sup>(3)</sup> The porphyrin dianion, formed by the removal of the inner NH protons, acts as a tetradentate ligand capable of binding a wide variety of metal ions. Metallation leads to a simplification of the visible region of the absorption spectrum, but little or no change to the B absorption. The B band (sometimes shifted depending on the metal) remains around 400 nm but the four Q bands in the visible region collapse to two bands labelled  $\alpha$  and  $\beta$  respectively.

Recent studies on the optical absorption and emission data have made it possible to class the metalloporphyrins into two broad classes depending on the metal ion present. The broad classes are known as REGULAR and IRREGULAR, the regular porphyrins containing only closed shell metals and the irregular partially filled shells.

### 2.2.1 Regular Metalloporphyrins

The regular metalloporphyrins consist of the metalloids from Groups I-V (in oxidation states I to II) and transition metals with electronic configurations  $d^0$  and  $d^{10}$ . They produce “normal” spectra i.e. a B band and two Q bands  $\alpha$  and  $\beta$ . This is indicative of little or no interaction between the metal orbitals and the porphyrin macrocycles  $\pi$ -orbitals. This regular porphyrin is one in which the optical and emission spectrum is determined by the  $\pi$ -electrons of the porphyrin ring, with only small perturbations from p- or d-electrons of the central metal ion.

### 2.2.2 Irregular Metalloporphyrins

For the irregular porphyrins, the metal orbitals have a much stronger effect on the absorption and emission spectral properties, either through stronger mixing with the ring orbitals or through the introduction of new low energy optical transitions. These unusual absorption types have been characterised into two; (i) hypso and (ii) hyper porphyrins:-

#### (i) Hypso Porphyrins

Hypso absorption spectra are similar to “normal” absorption spectra but are blue shifted. Such spectra are associated with the transition metal porphyrins of Groups VIII and IB with metal configuration  $d^{6-9}$  (4,5), in which the  $e_g$  ( $d\pi$ ) orbitals are filled. Octahedral ligand-field splitting of the metal d-orbitals produces  $t_{2g}$  and  $e_g$  states in which the orbitals comprising the  $t_{2g}$  state (i.e.  $d_x$ ,  $d_y$ ,  $d_z$ ) are filled. The  $d_{xz}$ ,  $d_{yz}$  orbitals of the metal overlap with the empty porphyrin  $\pi^*$  molecular orbitals allowing charge transfer from metal to porphyrin (Figure 2.4). This consequently raises the energy of  $\pi^*$  molecular orbitals, thus the charge-transfer from metal to macrocycle raises the energy of the porphyrin  $\pi$ - $\pi^*$  transition, with respect to metal-free porphyrins,

resulting in a hypsochromic (blue) shift in the spectrum. This metal to porphyrin charge transfer is known as 'back-bonding' and the effect increases with increasing atomic number e.g. Ni(II)<Pd(II)<Pt(II).<sup>(6,7)</sup>

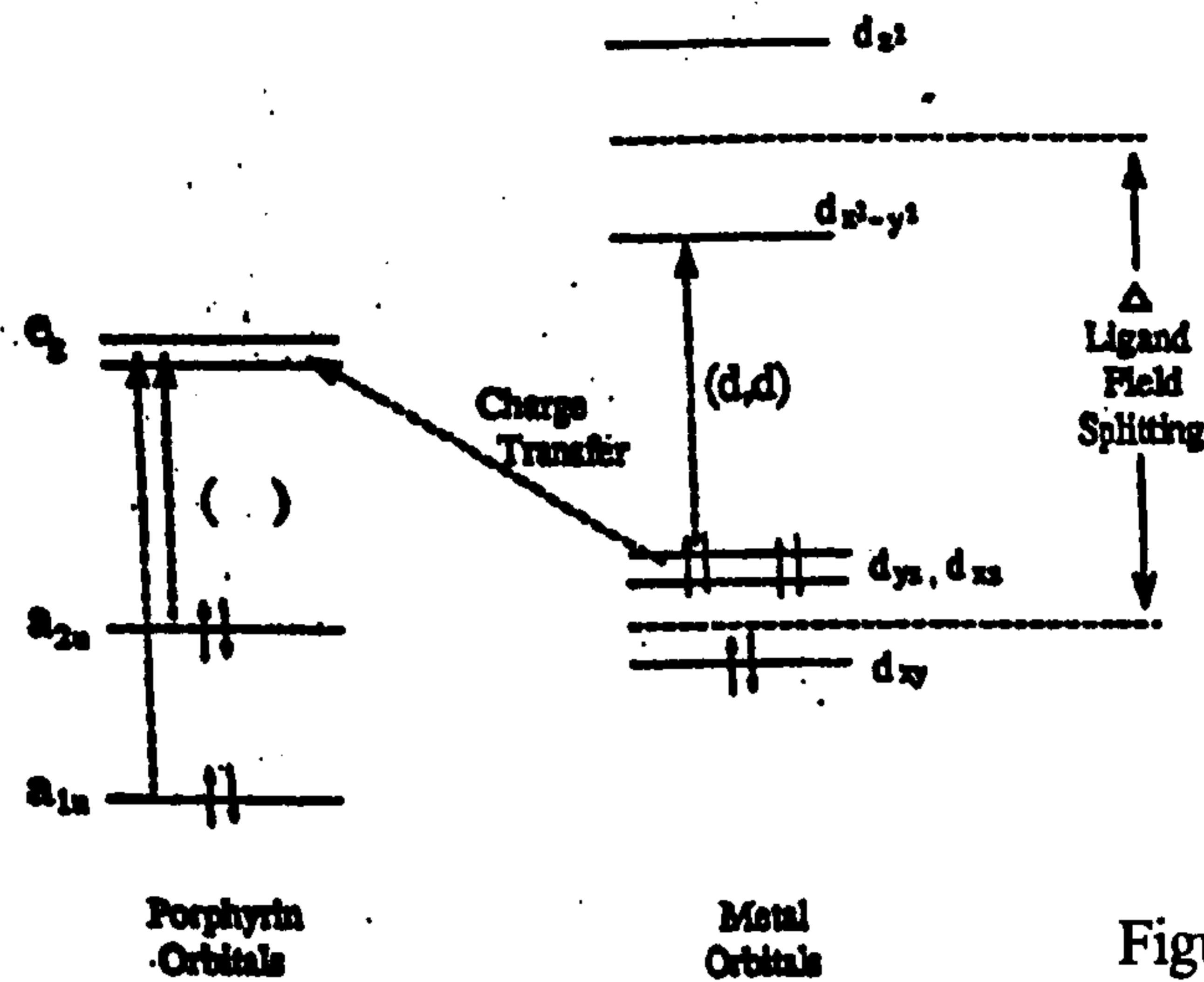


Figure 2.4

(ii) **Hyperporphyrins**

Hyper-type spectra are abnormal in that other intense absorptions in the region  $\lambda \sim 320$  nm, are observed in addition to the B and Q bands. These are divided into two subclasses:

(a) **p-type** - these are found with main group metals (Groups IIIA, IVA and VA) in low oxidation states (I-III), such as Sn<sup>II</sup>, Pb<sup>II</sup> and As<sup>III</sup>. The appearance of additional bands is due to the charge transfer from the partially filled metal p-orbitals into the porphyrin  $\pi^*$  orbital. As a consequence, the visible absorption is often considerably red shifted in comparison to other porphyrins.

(b) **d-type** - these are found in the transition metals with electronic configurations  $d^{1-6}$ , that have holes in the  $e_g$  ( $d\pi$ ) orbitals and relatively stable lower oxidation states. The extra bands arise from charge-transfer from filled porphyrin  $\pi$ -orbitals into vacancies in the metal orbitals comprising the  $t_{2g}$  state, i.e. there is ring-to-metal charge transfer.

## 2.3 Molecular Orbital Theory

A number of theories have been put forward in an attempt to explain the characteristic electronic spectra exhibited by porphyrin macrocycles. The theories tried to explain how band position, intensity and multiplicity changed from molecule to molecule.

Early models provided a reasonable interpretation as to why porphyrin macrocycles afforded the electronic spectra exhibited. However, the individual theories failed to explain all the phenomena associated with the electronic spectra.

The free electron theory<sup>(8,9)</sup> predicted the correct region of the spectra and the relative intensities of the respective bands but failed in its attempts to explain the multiplicity of the porphyrin Q bands.

The cyclic polyene theory<sup>(10,11)</sup> predicted the multiplicity of the respective bands but didn't take into account variations in the porphyrin's skeleton.

Huckel theory<sup>(12,13)</sup> was the first model to account for the porphyrin geometry. The simple Huckel LCAO (linear combination of atomic orbitals) approach was able to explain how the variations in the porphyrin's skeleton affected the optical transitions. However, Huckel theory failed to predict the relative intensities of the porphyrin B and Q bands.

The introduction of the molecular orbital theory for porphyrins has enabled accurate predictions for position, intensity and multiplicity for individual macrocyclic systems. Gouterman's "Four Orbital Theory"<sup>(14,15)</sup> has successfully accounted for many phenomena associated with porphyrin macrocycles, including the differences between the free base, metallated, di-cation and reduced ring porphyrin structures. The four orbital theory is a combination of

all the previously mentioned theories resulting in a model that could accurately predict the porphyrin's electronic spectra.

Huckel theory generated a set of molecular orbitals (Figure 2.5) in which singlet transitions can occur between the two highest occupied (HOMO) and the two lowest unoccupied (LUMO). Gouterman utilised this set of molecular orbitals generated by Huckel, the only difference was in how the orbitals were labelled. Gouterman relabelled the  $a_{1u}$  and  $a_{2u}$  to  $b_1$  and  $b_2$  respectively and  $e_g$  orbitals to  $c_1$  and  $c_2$ . This was introduced to allow systems with lower symmetry than the metalloporphyrins ( $D_{4h}$ ) to be considered.

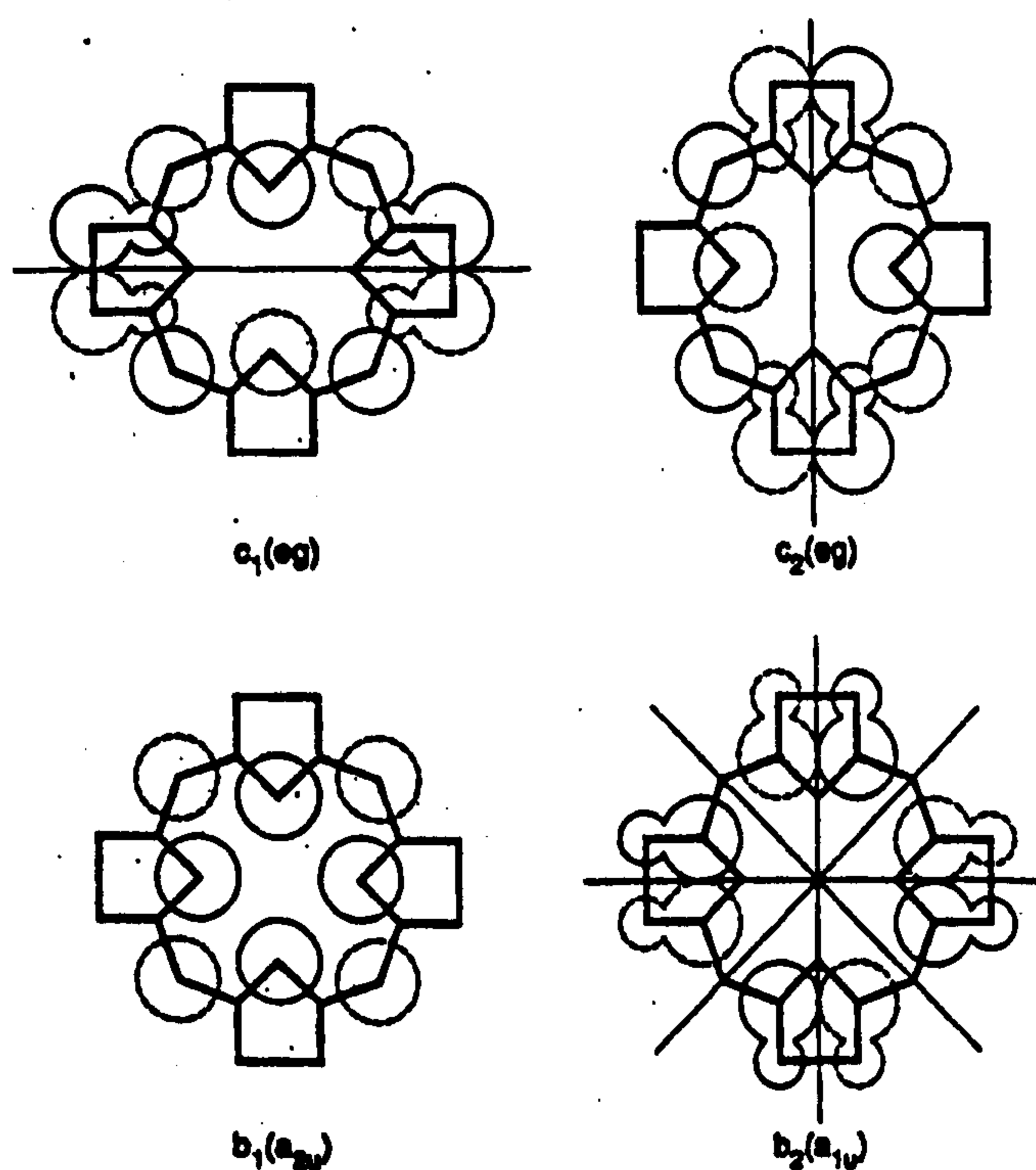


Figure 2.5

The MO theory predicts that electronic absorptions are brought about by the excitation of an electron from a filled orbital to an unfilled orbital. For the porphyrin system, this can be represented as a set of singlet transitions from  $b_1$ ,  $b_2$  to  $c_1$  and  $c_2$ . The introduction of configuration interaction<sup>(16)</sup>, generates a new set of terms by mixing them to give a sum and difference of their intensities which were originally equal. The sum and difference terms produced by mixing the configuration can be expressed:

$$\frac{b_1c_1 + b_2c_2}{\sqrt{2}} = B_y^0, \quad \frac{b_1c_2 + b_2c_1}{\sqrt{2}} = B_x^0$$

$$\frac{b_1c_1 - b_2c_2}{\sqrt{2}} = Q_y^0, \quad \frac{b_1c_2 - b_2c_1}{\sqrt{2}} = Q_x^0$$

where x and y are the directions of the components of the transition dipoles produced as a result of the excitation of an electron from the HOMO to LUMO. This results in a strongly allowed transition for  $B_y^0$  and  $B_x^0$  and a set of forbidden transitions  $Q_y^0$  and  $Q_x^0$ . Transitions  $Q_y^0$  and  $Q_x^0$  would be forbidden but for the vibrational coupling that destroys the degeneracy of the HOMO's  $b_1$  and  $b_2$ . This has the effect of lowering the symmetry for the molecule.

The MO theory is useful in that it can accurately predict the differences that occur upon metal insertion, di-cation formation and ring reductions. The theory exploits the difference in electron density each orbital possesses. Gouterman clearly shows that orbitals  $b_1$ ,  $c_1$  and  $c_2$  have electron density over the central nitrogens, whereas  $b_2$  doesn't. This difference in electron density is used to explain the characteristic spectra associated with the different porphyrin systems.

The relative intensities of the B and Q bands are dependent upon the interaction between the HOMO's and the LUMO's. The repulsive forces experienced on metal chelation has the effect of raising the orbital energy, whereas with di-cation formation, the attractive forces lower the energy. As a result, the lifting

of the degeneracy leads to the Q bands becoming more allowed and so increasing in intensity.

A similar interpretation can be used to predict the spectra of reduced porphyrins. The reduction of one of the peripheral double bonds has the effect of contracting orbitals  $b_2$  and  $c_1$  and as a result increasing their energies relative to  $b_1$  and  $c_2$ . This has an overall effect of intensifying the  $Q_y$  band.

## 2.4 Nuclear Magnetic Resonance Spectroscopy

### 2.4.1 Introduction

Since the rapid development of proton nuclear magnetic resonance (n.m.r.) spectroscopy, it has been used as a powerful tool to gain a wealth of information about the porphyrin macrocycle.<sup>(17)</sup> This is brought about mainly due to the fact that the macrocycle has a large built in ring current<sup>(18,19)</sup>. The ring current functions as a built in chemical shift reagent, resulting in nmr spectra ranging over 15 p.p.m. This spreading of n.m.r. spectra enables a more simplified interpretation and assignment for the porphyrin macrocycle.

The first  $^1\text{H}$  nmr spectra of porphyrins were reported by Becker and Bradley.<sup>(18)</sup> Following extensive synthetic work by Jackson, Kenner and Smith,<sup>(20)</sup> a series of researches was carried out by Abraham on a number of special aspects of porphyrin behaviour including the effects of substitution,<sup>(21,22)</sup> self-aggregation in solution<sup>(23,24,25)</sup> and isomerism of porphyrins.<sup>(26)</sup>



### 2.4.2 The Theory of nmr

The only nuclei that exhibit the nmr phenomenon are those for which the spin quantum number  $I$  is greater than 0: the spin quantum number  $I$  is associated with the mass number and atomic number of the nuclei as follows:

Mass Number	Atomic Number	Spin Quantum Number
odd	odd or even	$1/2, 3/2, 5/2$
even	even	0
even	odd	1,2,3

The nucleus of  $^1\text{H}$  has  $I = \frac{1}{2}$ , and under the influence of an external magnetic field the magnetic nucleus can take up different orientations with respect to that field; the number of possible orientations given by  $(2I + 1)$ . The nuclei of most interest in porphyrin chemistry ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{15}\text{N}$ ) having  $I = \frac{1}{2}$  will have two such allowed energy levels.

In an applied magnetic field, magnetic nuclei process at a frequency  $\nu$ , which is proportional to the strength of the applied field. The exact frequency is given by

$$\nu = \left( \frac{\gamma}{2\pi} \right) H_0$$

There are three parameters which are obtained from the nmr spectrum; (1) frequency of the energy absorption (chemical shift,  $\delta$  in ppm), (2) the splitting (J in Hz) of the absorption signal resulting from spin-spin interactions and (3) the intensity of the absorption signal, which is a measure of the number of nuclei associated with a particular line in a spectrum.

Different proton peaks arise in the spectra due to the fact that each particular proton does not experience the net external magnetic field applied, but a magnetic field modified by its particular environment. The additional local magnetic field produced by neighbouring nuclei with magnetic properties are proportional to  $H_0$  and can be expressed as:

$$\nu = \left( \frac{\gamma}{2\pi} \right) H_0 (1 - \sigma)$$

where the shielding constant  $\sigma$  is a measure of the modification of the external magnetic field  $H_0$  by the chemical environment.

In practice chemical shifts are given with respect to some reference compound, the most commonly used being tetramethylsilane (TMS). The chemical shift ( $\delta$ ) is measured in parts per million (ppm) and its relationship with the frequency (Hz) can be expressed as:

$$\delta_x = \frac{\nu_x - \nu_{\text{TMS}}}{\nu_0}$$

$\delta_x$  = chemical shift

$\nu_x$  and  $\nu_{\text{TMS}}$  = frequencies for the signals x and tms.

$\nu_0$  = operating frequency of the instrument.

### 2.4.3 NMR of Porphyrins

In the  $^1\text{H}$  nmr spectra of porphyrins, the long range diamagnetic contribution of the aromatic macrocyclic system to the chemical shift, is the most important factor. The circulation of the electrons (ring current) gives rise to a secondary magnetic field which then produces an anisotropic shielding effect on the protons within the range of the ring current. The magnetic shielding resulting from the ring current is positive for nuclei on the outside of the loop, and negative for nuclei within. The  $\beta$ -pyrrolic proton resonances of the free base porphyrin appear around 9 ppm (relative to TMS), whereas the N-H resonances occur upfield (-2.7 ppm) due to strong shielding caused by the aromatic ring current. These resonance peaks are substantially different when compared to pyrrole, the peripheral protons shifting 5 ppm down field and the inner N protons 11 ppm upfield.

Almost any structural modification to the macrocyclic system changes its ring current and hence changes in the chemical shift. Some general observations have been applied to porphyrins and their change in ring current:

- (1) The ring current is larger in both neutral complexes and di-cations due to the increased resonance stabilisation of these compounds<sup>(19)</sup>.
- (2) Steric hindrance causes a decrease in the ring current due to the reduction of the  $\pi$ - $\pi$  overlap by distorting the planar macrocycle structure. This factor is enhanced by N-substitution and meso-substitution.
- (3) A decrease in the electron density of the  $\pi$ -system diminishes the ring current and may then cause up field proton shifts. This is the opposite effect where a decrease in electron density generally leads to a reduced shielding and down field shifts.

Therefore, it can be said that detailed predictions of porphyrin nmr spectra can be obtained by applying these observations. The effects of substituents on the porphyrin periphery can lead to vast differences depending on the electron donating or electron withdrawing effect and the steric hindrance considerations.

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25. Abraham, R.J., Barnett, G.H., Bretschneider, E.S., Smith, K.M., Tetrahedron, 29, 553 (1973).
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### **3 PORPHYRIN APPLICATIONS**

#### **3.1 Introduction to Nonlinear Optics**

Nonlinear optics is the study of the interaction of intense laser light with matter<sup>(1,2)</sup>. Laser light is sufficiently intense to affect the optical properties within a material.

As light passes through a material, its electric field interacts with the electric fields within the material and as a result, cause the material's properties to change<sup>(3)</sup>. The interactions that exist between the various fields have a major effect on the polarization of the material.

#### **3.2 Polarization**

Polarization is the average electric dipole moment per unit volume of a sample. In the absence of an applied field, the molecules adopt a random orientation, and hence, have a polarization equal to zero. In the presence of an electric field, the dipoles become partially aligned and result in the polarization becoming non-zero. In order to understand the concept of nonlinear optics, we need to understand how the polarization of a material depends on the introduction of an applied field.

Polarization of electron density away from the nucleus results in an induced dipole moment  $\mu$ . In the presence of an electric field that is not too strong, the magnitude of the induced dipole moment is proportional to the field E (1).

$$\text{Polarization} = \mu = \chi E \quad (1)$$

where the constant  $\chi$  is equal to polarizability of the material.

As shown in Figure 3.1, the plot of polarization against the applied field results in a straight line whose slope is equal to  $\chi$ .

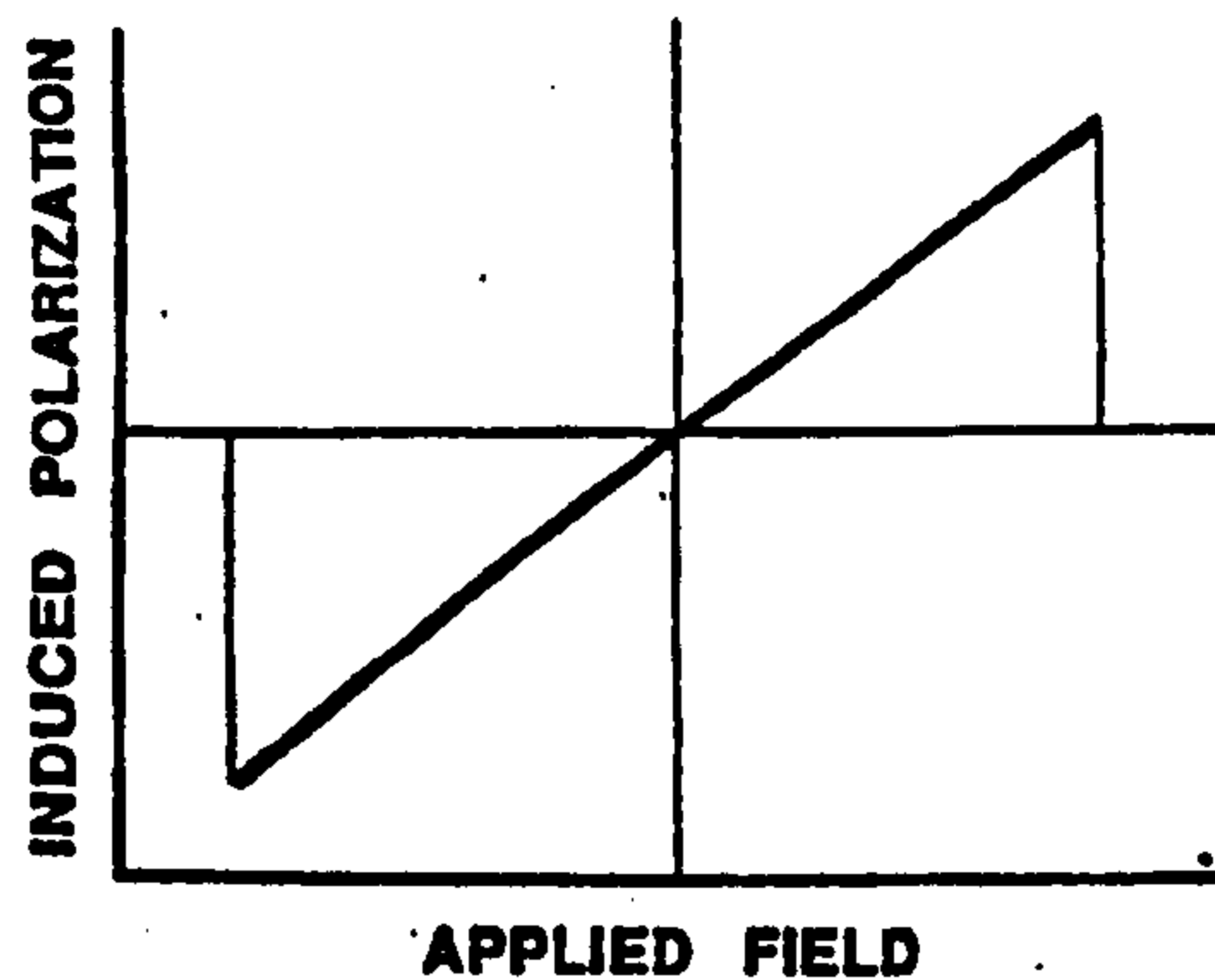


Figure 3.1 Plot of induced polarization versus applied field.

It is also important to consider the refractive index ( $n$ ) of a material since this property is unique for each material or substance. The refractive index of a medium is the ratio of the speed of light in a vacuum  $c$  to its speed  $v$  in the medium (2).

$$n = c/v \quad (2)$$

where  $c$  = speed of light in a vacuum.

$v$  = speed of light in a material.

The polarisability constant ( $\chi$ ) is related to the refractive index ( $n$ ) by the expression:

$$n^2 = \chi + 1 \quad (3)$$

For a linear medium both  $\chi$  and  $n$  are material constants for a given temperature and pressure.



It is evident that the chemical structure of a material is extremely important, since the optical properties depend considerably on the electron distribution of a material. Therefore, any alterations to the chemical structure will have notable effects on the optical properties.

### 3.3 Nonlinear Polarizability

In the previous section, we have shown that the polarization of a material is a linear function of the applied field. However, in the presence of a strong applied field, the induced polarization produces an internal field that modifies the applied field and the subsequent polarization.

As shown in Figure 3.2, in a nonlinear optical material, the proportionality between force (electric field) and response (polarization) no longer exists.

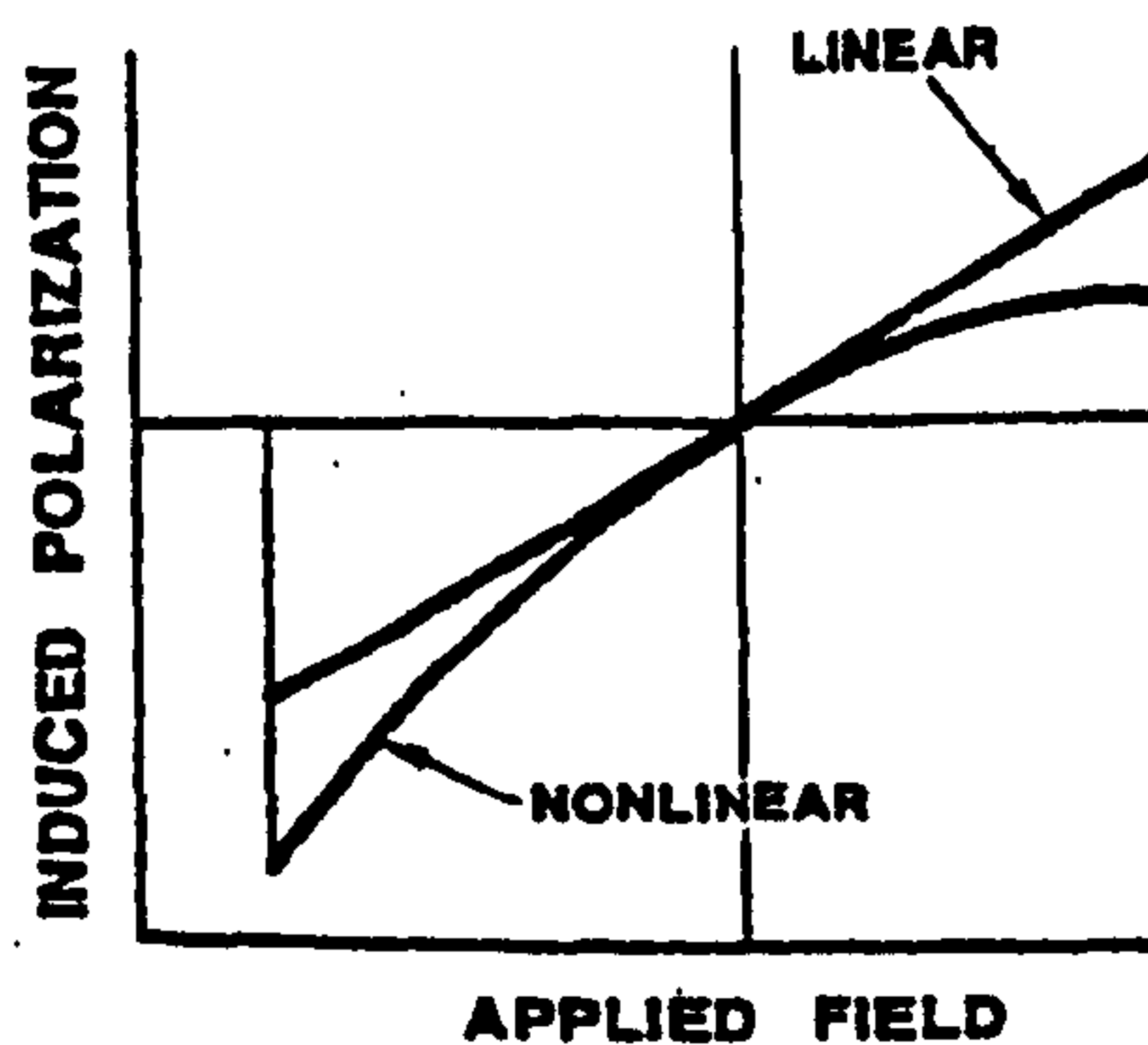


Figure 3.2

It is now usual to express  $P$  in terms of powers of the field  $E$ :

$$P = \mu = \chi_1 E + \chi_2 E^2 + \chi_3 E^3 + \dots \quad (4)$$

$\chi_1$  = Linear polarizability

$\chi_2 + \chi_3$  = second order and third order hyperpolarizabilities and so on.

### 3.4 Second-order Nonlinear Optical Processes

Even order electric dipole coefficients are zero for centrosymmetric molecules, and as a result, organic molecular structures must be non-centrosymmetric for them to exhibit second-order nonlinear optical effects. This can be achieved by introducing electron donor and acceptor groups at diametrically opposed positions in the structure. Understanding the basic physical mechanisms of nonlinear optical processes has led to the development of efficient computational methods that allow the exploration of second-order optical properties of  $\pi$ -conjugated structures.<sup>(4)</sup> For many structures theoretical calculations reveal that large second-order effects result from highly asymmetric, charge-correlated excited states. Often the main contribution to the second-order susceptibility,  $\beta$ , results from the first  $\pi$ -electron excited state. On excitation electron density from the electron-donor region is transferred to the electron acceptor, resulting in a large charge separation and an associated large optical transition moment. There are three key parameters that determine  $\beta$ :

- (I) the transition energy
- (II) the dipole moment difference and
- (III) the transition moment between the ground state and first  $\pi$ -electron excited state.

Therefore, to enhance  $\beta$ , it is necessary to decrease the transition energy and increase the two moment parameters. Two such ways to achieve this is by increasing the strength of the electron-donor and acceptor substituents and to increase the conjugation length of the  $\pi$ -bridge that separates the donor-acceptor groups.

Such requirements are thus, best met by dipolar, highly polarizable, donor-  $\pi$  acceptor systems, showing charge transfer between electron-donating and electron withdrawing groups. Considerable work<sup>(7,8,9)</sup> has been carried out to

find the optimum combinations of acceptor and donor groups, with particular interest in organic compounds that are easily substituted. Reports have concluded that the first hyperpolarizability ( $\beta$ ) increases with increasing conjugation length but that the strongest acceptor does not necessarily lead to the largest nonlinearity.<sup>(9)</sup> Also for a known combination of donor-acceptor groups, there exists an optimum conjugated  $\pi$  chain length, above which the  $\beta$  values decrease.<sup>(10,11,12)</sup> A significant enhancement of polarizability has been observed by extending the conjugation length between donor and acceptor. This generally results from decreasing the energy gap and increasing the transition dipole moment between the relevant states. Studies<sup>(13,14,15)</sup> of various conjugated backbones have been previously well documented.

There are two main techniques in operation for second-order NLO; linear electro-optic (LEO)<sup>(5)</sup> effect and second harmonic generation (SHG).<sup>(6)</sup> The LEO effect is a second-order optical process in which an externally applied dc or low frequency electric field couples to the optical electric field causing a change to the refractive index ( $n$ ) of the material. This change in  $n$  leads to a change in phase or polarization of the light beam that can be converted into a change in intensity of the beam using a polarizer. This measurement gives a value of LEO coefficient,  $r$ , that is related to the second-order susceptibility,  $\chi^2$  ( $-\omega, 0, \omega$ ).

$-\omega$  = frequency of output

$0$  = dc electric field

$\omega$  = input light field.

The other common technique used is second-harmonic generation (SHG). In a SHG measurement a laser beam at frequency  $\omega$  illuminates a sample and coherent light at twice the frequency  $2\omega$  is generated and detected. This is illustrated schematically in Figure 3.3.

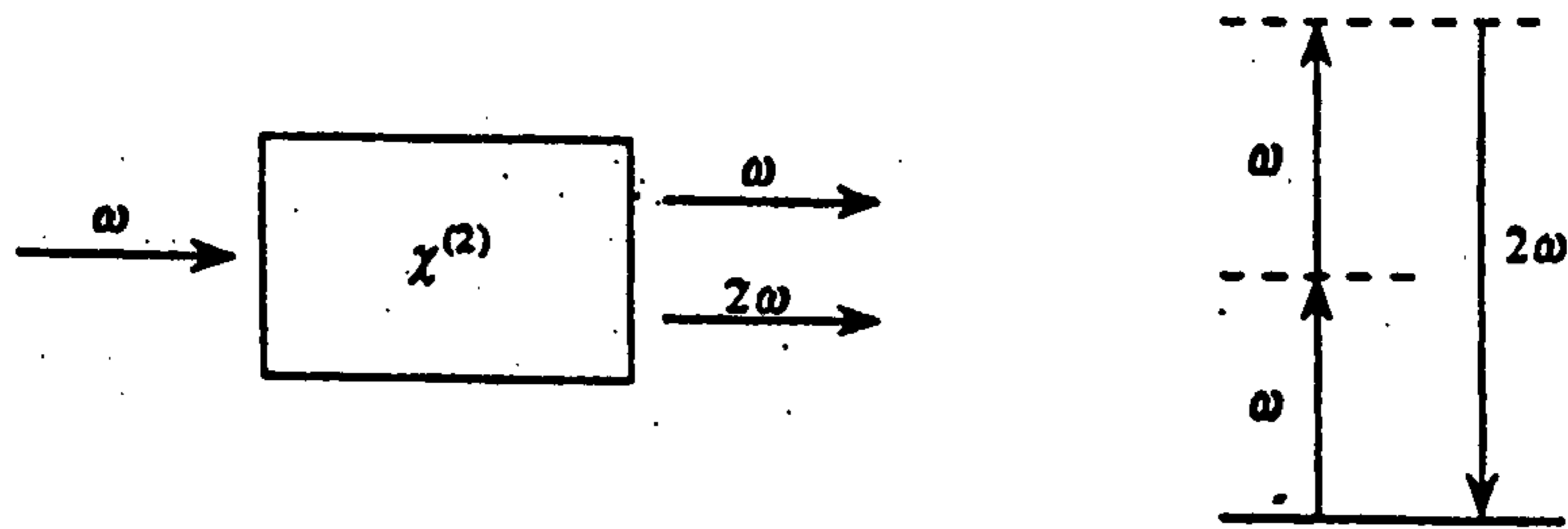


Figure 3.3

In addition to the sample types used in the LEO experiments, measurements can be performed on powdered samples.

### 3.5 Third-order Nonlinear Optical Processes

The structure property relationships that govern third-order NLO polarization are not so well documented. Unlike the design of second-order NLO materials, models for the synthesis of third-order species are much less well-developed. Although the understanding of structure-property relationships for third-order effects is limited, materials possessing a large delocalised  $\pi$ -electron backbone are considered to give large third-order results.<sup>(16,17)</sup> These molecular structures do not have to be asymmetric because  $\gamma$  is a fourth rank tensor, therefore, third-order optical effects occur naturally in all optical media.

Organic materials with extended  $\pi$ -conjugation are known to be important, and an increased effective conjugation and hence, large  $\pi$ -delocalisation length has been recognised as a way of achieving large third-order nonlinearities.<sup>(18-20)</sup>

To date, a majority of the work regarding third-order nonlinearities has been centred around polymers. Conjugated polymers with alternate single and multiple bonds in their backbone structure provide long  $\pi$ -electron conjugated structures which are ideal for  $\chi^3$ .<sup>(21)</sup> These organic systems have undergone

extensive research, so consideration must be given to developing new systems that have extended  $\pi$ -electron delocalisation.

Early work concerning organic compounds gave maximum nonlinearities around  $10^{-9}$  to  $10^{-8}$  esu, but these are many orders of magnitudes lower than those of the inorganic semiconductor systems, raising the question as to whether they are of any use. However, organic compounds have some points in their favour.

Firstly, because the process responsible for the nonlinearities in the organic compounds are not dependent on a real excitation of the molecule, they are not specific to a particular wavelength, and so the materials can be used at any point of the spectrum where they do not absorb the incident or emitted light. Secondly, because there is no direct involvement of excitation and relaxation processes, the response times of these materials can be very fast and are only limited by the electronic response times.

There is a wider range of third-order techniques commonly used to characterise materials. They include: electric field induced second harmonic generation (EFISH),<sup>(22, 23)</sup> third harmonic generation (THG)<sup>(24)</sup> and degenerate four wave mixing (DFWM).<sup>(25)</sup>

EFISH involves the generation of a second harmonic wave in a material that is subjected to an applied D.C. electric field. The process involves the third-order susceptibility  $\chi^3$   $(-2\omega; 0, \omega, \omega)$ , and can be performed on gaseous, liquid or solid samples. Even though the process involves SHG, EFISH is a third-order process.

DFWM is a third-order process involving the nonlinear susceptibility  $\chi^3$   $(-\omega; \omega, -\omega, \omega)$ . In the DFWM, measurement, three beams at frequency  $\omega$  intersect the material. The nonlinear interaction produces a fourth beam at the

same frequency and its intensity is proportional to the product of the input intensities and the absolute square of  $\chi^3$ .

Third harmonic generation (THG) is the generation of light at frequency  $3\omega$  by the nonlinear interaction of a material and a fundamental laser field at frequency  $\omega$ . The process involves the third-order susceptibility  $\chi^3(-3\omega; \omega, \omega, \omega)$  where  $-3\omega$  represents an output photon at  $3\omega$  and the three  $\omega$ 's stand for the three input photons at  $\omega$ . Since  $\chi^3$  is a fourth rank tensor property it can be non zero for all material symmetry classes.

### 3.6 Reverse Saturable Absorption

Reverse saturable absorption in organic molecular materials was first described in 1967<sup>(26)</sup> and included the compounds sulphonated indanthrone and sudan schwarz B. These were discovered as a result of work carried out on saturable absorbers. Since this discovery a number of compounds have been investigated, which include spiropyrans,<sup>(27)</sup> metal cluster compounds,<sup>(28)</sup> phthalocyanine<sup>(29)</sup> and tetraphenylporphyrins.<sup>(30)</sup>

The availability of high intensity laser light sources has resulted in research into materials whose absorption of radiation is nonlinear (i.e. disobeys the Beer-Lambert law). Organic molecular compounds, especially dye compounds, have shown considerable potential for this.

Nonlinear absorption has two desired effects:

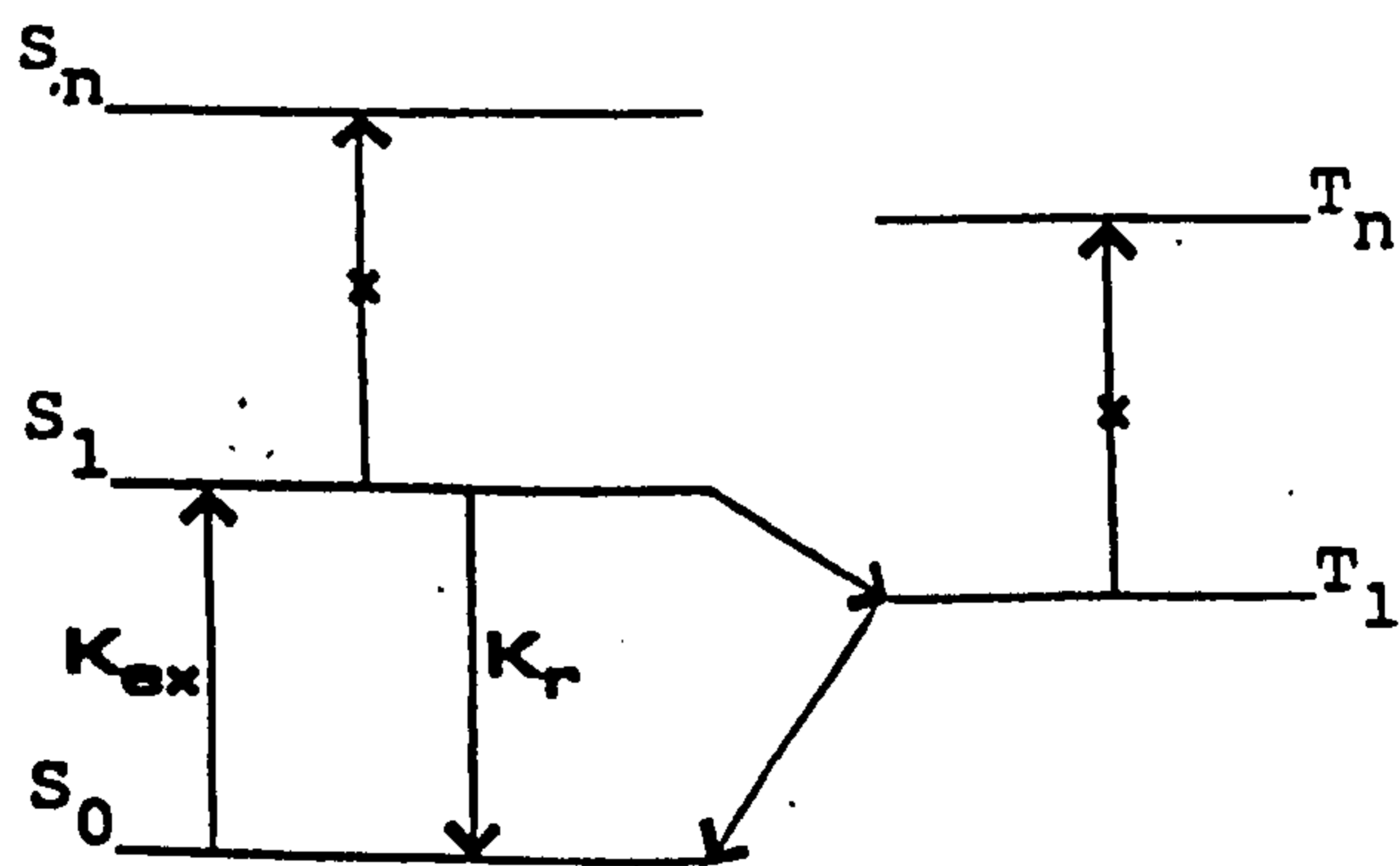
- (I) Transmitted light intensity increases with increasing light intensity (saturable absorption or optical bleaching).
- (II) Transmitted light intensity decreases with increasing light intensity (reverse saturable absorption).

For a molecule to be suitable as a nonlinear absorber, it must exhibit stability to photochemical destruction caused by high intensity laser radiation.

Since reverse saturable absorption is the subject of interest, this will be looked at in greater detail, but a brief description of saturable absorption is necessary.

(i) **Saturable absorption** <sup>(31)</sup>

A saturable absorber is a molecule in which the ground and excited state cross-sections are essentially equal under high power laser radiation. Thus the rate of transition by absorption equals the rate of relaxation by stimulated emission. The first case requires three energy levels (Figure 3.4). A transition from the ground-state to the first excited state is followed by radiationless decay to the lowest possible first excited state. Then relaxation with stimulated emission occurs back to the ground state. Saturable absorption occurs when the rate of excitation equals the rate of relaxation. Optical bleaching occurs when molecules decay from the first excited state to a metastable excited state followed by subsequent relaxation to the ground state.



- s = singlet state
- t = triplet state
- $K_{ex}$  =  $K_r$  for saturable absorption
- x = does not occur in saturable absorbers.

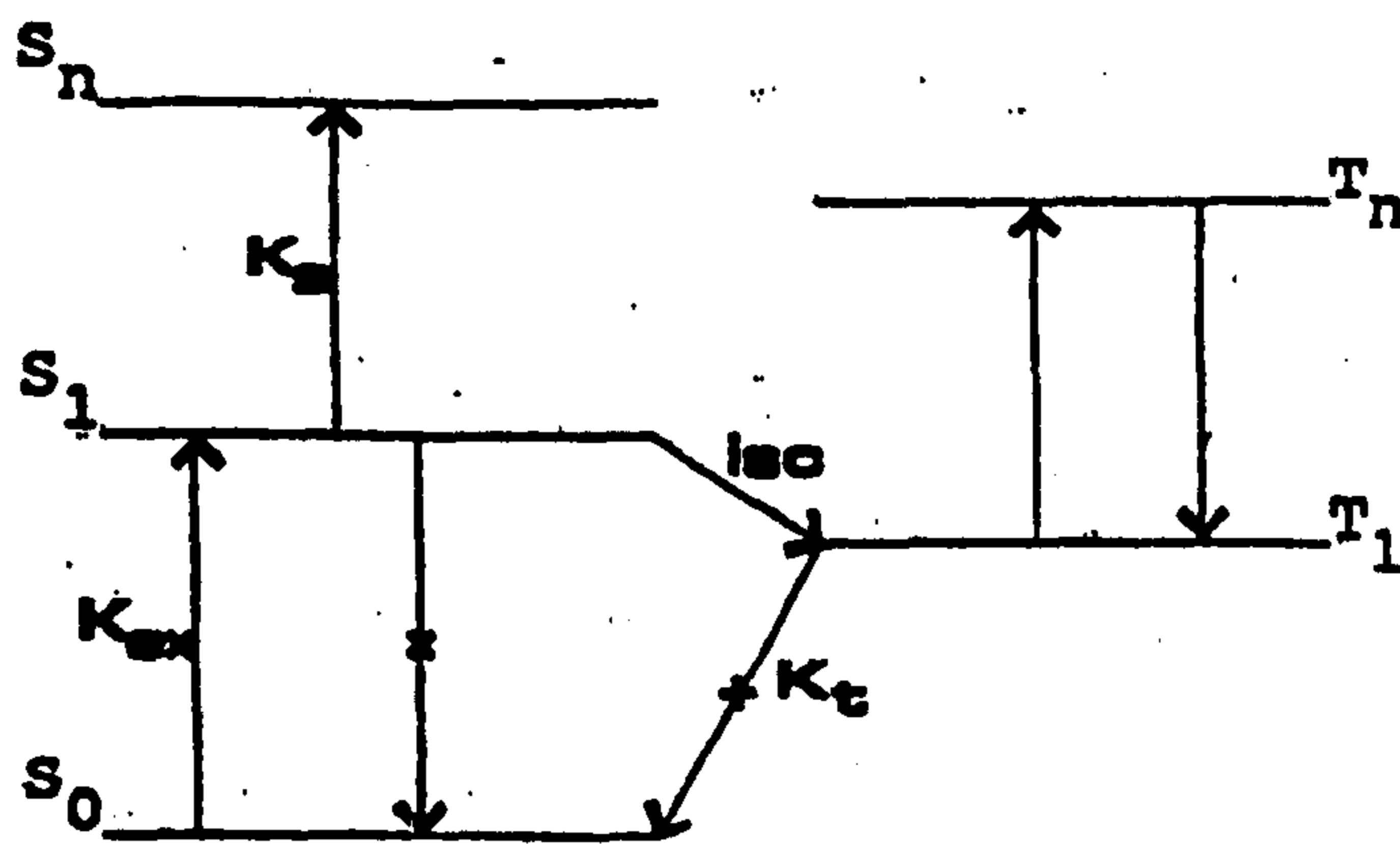
Figure 3.4

**(ii) Reverse saturable absorption <sup>(32)</sup>**

Reverse saturable absorption (RSA) occurs in molecules where the excited state absorption cross-section, at wavelength  $\lambda$ ,  $\sigma_{ex}(\lambda)$  exceeds the ground-state absorption cross-section  $\sigma_{gr}(\lambda)$  under intense radiation. The criteria for a molecule to be a successful RSA are: (1)  $\sigma_{ex}(\lambda) > \sigma_{gr}(\lambda)$  as mentioned, (2)  $\sigma_{gr}(\lambda)$  sufficiently large so the incident pulse saturates the first excited state, (3) neither the first excited state nor the higher-lying excited state should decay to other levels which trap the excitation, (4) the emission cross-section  $\sigma_{em}(\lambda)$  should be small.

At a particular laser wavelength, ground-state absorption results in molecules occupying higher vibrational levels of the first excited electronic state. The population in the first excited state rapidly decays nonradiatively to the lowest energy levels of the first excited state manifold. Thus, the energy for the transition from first to second singlet excited states must be within the range of the laser radiation energy. The excited state absorption cross-section  $\sigma_{ex}$  resulting from absorption from the first excited state to higher lying electronic states, must be higher than the cross-section of ground state to first excited state transitions for reverse saturable absorption to occur. Relaxation from first excited states to ground state should not be favoured so that excited states may be populated. Also, higher electronic excited states should rapidly decay back to the lowest excited state, so that this transition does not saturate.





$k_{ex} < k_s$  and  $k_t = 0$  for reverse saturable absorption  
 $X^{ex}$  does not occur in reverse saturable absorbers  
 ISC = intersystem crossing.

Figure 3.5

If saturable and reverse saturable absorbers are used in conjunction, they may be used to mode lock lasers whereby the saturable absorber cuts the leading edge of the pulse and the reverse saturable absorber cuts the trailing edge.<sup>(33)</sup> The same combination is utilised for optical compressors<sup>(34)</sup> in a laser amplifier by eliminating the edges of short pulses produced as a result of superfluorescence and superradiance.

Reverse saturable absorbers may also display optical bistability (i.e. may be stable in two different states, as in a switch).<sup>(35)</sup>

### 3.7 Porphyrins for nonlinear optical and reverse saturable absorption applications

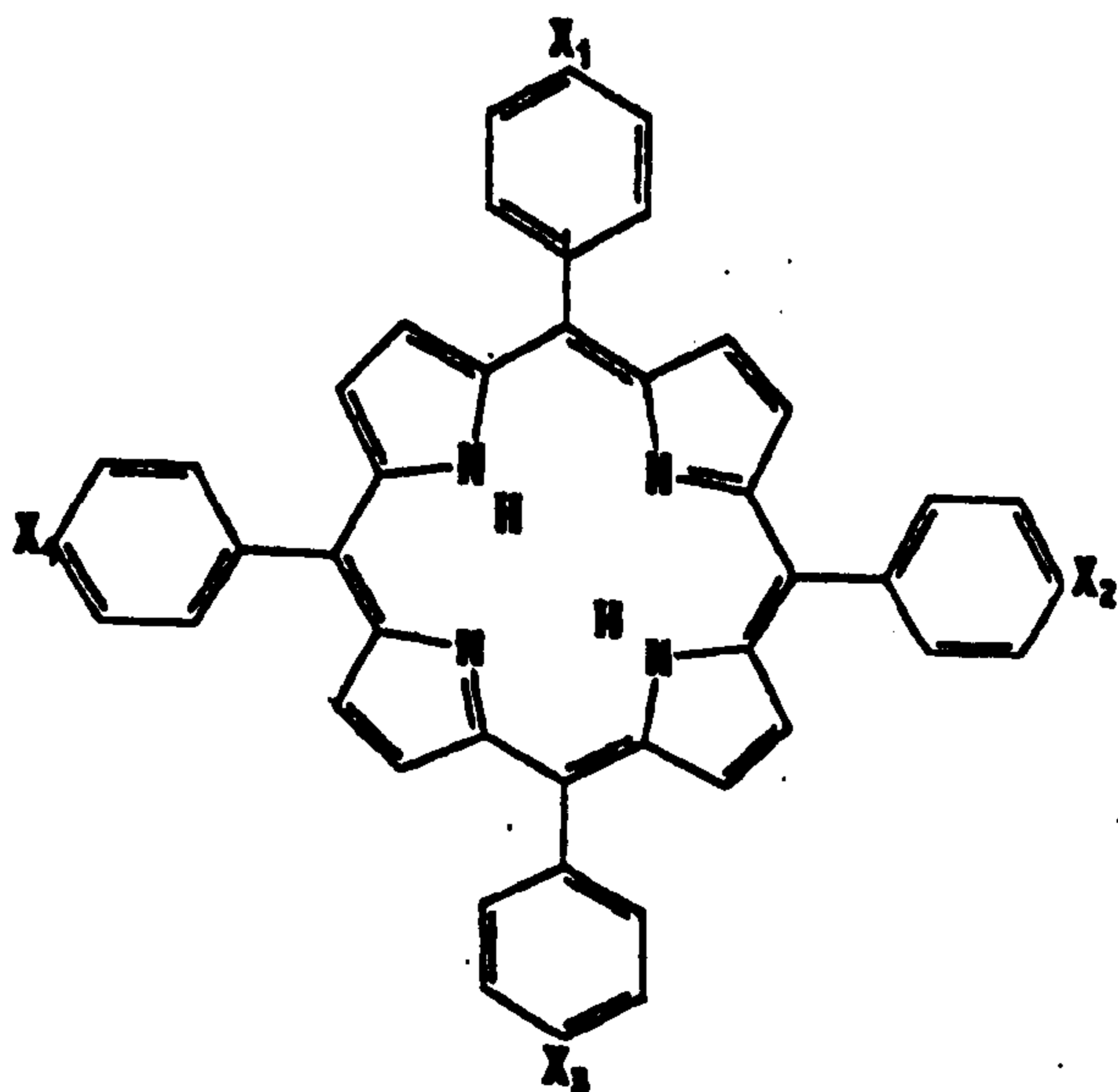
The nonlinear optical properties of organic molecules are of great interest,<sup>(36,37)</sup> with considerable attention being given to porphyrins and their derivatives.

Extensively delocalised cyclic  $\pi$ -systems, such as phthalocyanines and porphyrins, are studied as third order NLO materials<sup>(38,39)</sup> due to their symmetric structures in nature. Introduction of porphyrins which lack a centre of symmetry has led to compounds that possess second-order NLO properties.

Porphyrins are attractive building blocks as NLO materials owing to their large polarizable  $\pi$ -systems and their wide range of metal ions. The meso-tetraphenylporphyrins (TPP) have been shown to be useful starting materials and exhibit interesting optical characteristics in the variety of solvents in which they are soluble.

Structural modification of TPP by varying the central metal ion and/or substitution of organic donor-acceptor (D-A) groups, has led to a two-dimensional network for effective intramolecular charge transfer (ICT). This fine tuning of porphyrin structures has led to compounds that possess moderately high second-order NLO properties.

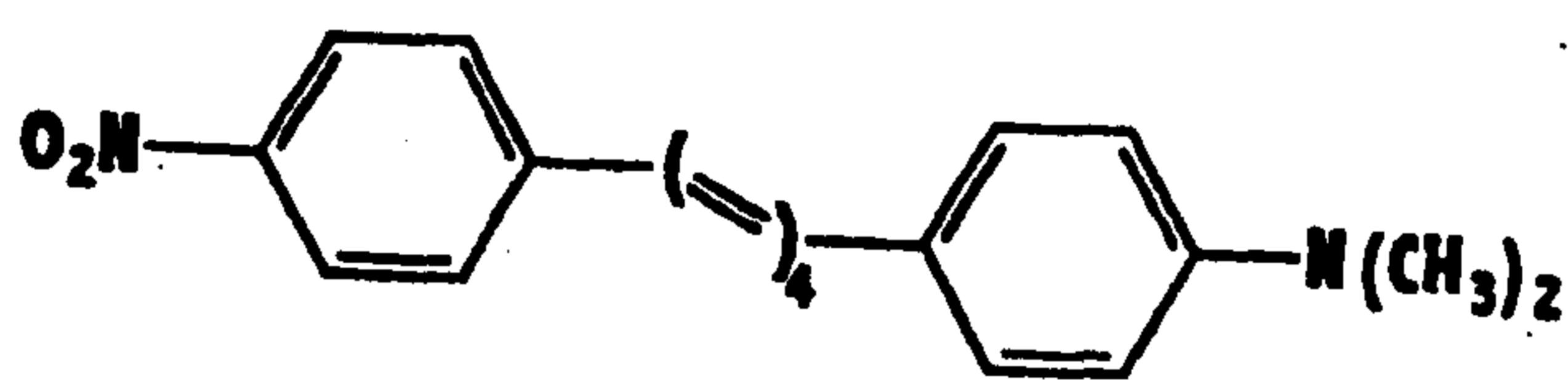
Early work involving second-order NLO materials was carried out by Suslick et al<sup>(40)</sup> and this was centred around the unsymmetrically substituted aminonitrotetraphenyl free-base porphyrins. Synthesised by the partial reduction of the nitro groups of 5,10,15,20-tetrakis-(p-nitrophenyl) porphyrin<sup>(41)</sup> Suslick produced the unsymmetrical porphyrins H<sub>2</sub> (a<sub>3</sub> Por)[4], H<sub>2</sub> (a<sub>3</sub> nPor)[6], H<sub>2</sub> (trans-a<sub>2</sub>n<sub>2</sub>Por)[7] and H<sub>2</sub>(cis-a<sub>2</sub>n<sub>2</sub>Por)[5] where n denotes nitro and a amino respectively (Figure 3.6).



- [4] X<sub>1</sub>=X<sub>2</sub>=X<sub>3</sub>=NO<sub>2</sub> , X<sub>4</sub>=NH<sub>2</sub>
- [5] X<sub>1</sub>=X<sub>2</sub>=NO<sub>2</sub> , X<sub>3</sub>=X<sub>4</sub>=NH<sub>2</sub>
- [6] X<sub>1</sub>=X<sub>2</sub>=X<sub>3</sub>=NH<sub>2</sub> , X<sub>4</sub>=NO<sub>2</sub>
- [7] X<sub>1</sub>=X<sub>3</sub>=NH<sub>2</sub> , X<sub>2</sub>=X<sub>4</sub>=NO<sub>2</sub>

Figure 3.6

As already mentioned, organic molecules with strong electron donor and electron acceptor groups that are connected by a large conjugated  $\pi$ -electron system usually show high  $\beta$  values. Suslick et al reported results where the first hyperpolarizabilities were lower ( $\beta = (10-30) \times 10^{-30}$  esu) than that expected for such a large cyclic  $\pi$ -system. When the first hyperpolarizability results are compared with a previously tested linear tetraene [8] (Figure 3.7) ( $190 \times 10^{-30}$  esu), it can be seen they are considerably lower.



[8]

Figure 3.7

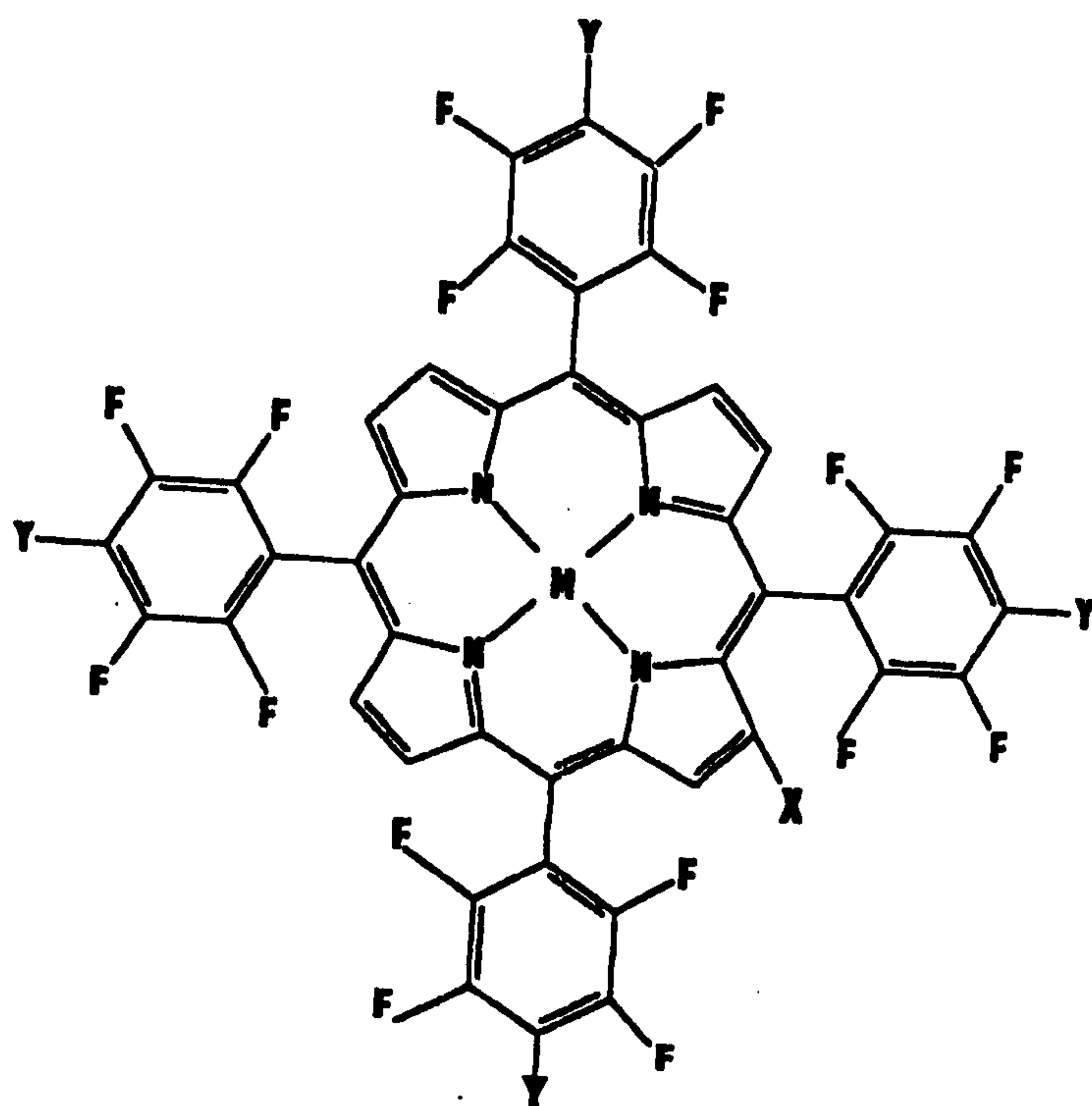
This can be accounted for by the fact the porphyrin structure with its additional dimensionality in a direction perpendicular to the principal axis actually has the effect of reducing the overall NLO response.<sup>(42)</sup> Also unfavourable orientation of the meso aryl groups (which incorporate the amino and nitro groups) with reference to the porphyrin plane also reduces the CT interactions between the push and pull groups of these desired porphyrins.

The  $\beta$  values for the above mentioned “push-pull” porphyrins vary considerably between themselves ( $10-30 \times 10^{-30}$  esu). Despite the similarity between the dipole moments of their ground states,  $H_2(an_3Por)$  and  $H_2(a_3nPor)$  are not equivalent in the charge transfer behaviour of their excited states. Electron donating  $NH_2$  groups push substantially less charge into the conjugation system than the accepting  $NO_2$  groups withdraw in the excited CT states. For  $H_2(a_3nPor)$  charge is donated by three donors and, in the excited CT state, pulled by one strong acceptor giving a relatively high  $\beta$  value. For  $H_2(an_3Por)$  only one donor group pushes charge into the macrocycle, while this charge is drained by three strong acceptors, this resulting in a lower  $\beta$  value. This can

also explain why  $H_2(\text{Cis-a-2n}_2\text{Por})$  has the largest  $\beta$  value of the three porphyrin systems.

One other factor has to be considered in the potential of “push-pull” porphyrins, and that is, tetraarylporphyrins have a less effective ICT due to the dihedral twist between phenyl rings and the plane of the porphyrin. Due to this steric hindrance, the phenyl ring is expected to be out of the plane of the porphyrin and this has an effect of lowering the  $\beta$  values.<sup>(43)</sup>

Krishnan et al<sup>(44)</sup> attempted to synthesise porphyrin structures [9-12], whereby the nitro-acceptor group was situated on the pyrrole ring (Figure 3.8) in an attempt to increase the ICT between the donor-acceptor groups.



	<b>X</b>	<b>Y</b>
[9]	<b>H</b>	<b>F</b>
[10]	<b>H</b>	<b>NMe<sub>2</sub></b>
[11]	<b>NO<sub>2</sub></b>	<b>F</b>
[12]	<b>NO<sub>2</sub></b>	<b>NMe<sub>2</sub></b>

Figure 3.8

$\beta$  values reported for these compounds exhibit moderate second-order nonlinearity ( $12 - 32 \times 10^{-30}$  esu). The relatively lower result for (9) can be explained due to its nonzero dipole moment and its symmetrical substitution with the phenyl rings not in the same plane as the porphyrin. The  $\beta$  values are dependent on the nature and position of substituents, and introduction of four amino groups increases the  $\beta$  value but not as much as expected. This again is due to steric constraints enforced by the position of the phenyl ring and this has a direct effect on the interaction of the phenyl rings with the macrocyclic  $\pi$ -pathways, resulting in lower  $\beta$  values.

Introduction of the nitro group at one of the pyrrole carbons has the affect of increasing the  $\beta$  values since this group is now situated in the conjugative pathway. This is evident in comparison of the  $\beta$  values of (10) and (11). The  $\beta$  value of (11) is higher than that of (10) even though (10) incorporates four strong donor groups. The effectiveness of the CT interaction between the nitro (acceptor) and the donor group is evident by the higher  $\beta$  value experienced by (12).

As experienced by Suslick et al,<sup>(40)</sup> the  $\beta$ -values observed are moderately high but low in comparison to those reported for the D-A acyclic trienes.<sup>(45,15)</sup> A reason for this could be that in cyclic  $\pi$ -conjugation the effective path length for  $\pi$ -electron delocalization is reduced. Charge transfer interaction between donor and acceptor through a  $\pi$ -electron backbone is most favourable when the double bonds are all of the trans configuration.<sup>(46)</sup>

More recently, both electron-releasing and electron-withdrawing groups fixed via an intervening ethynyl moiety attached directly to the porphyrin macrocycle have been synthesised to reduce this problem.<sup>(47)</sup> Initially a variety of ethynyl porphyrin arrays were synthesised by Therien et al<sup>(48)</sup> (Figure 3.9) and these compounds exhibited relatively high second-order NLO results.

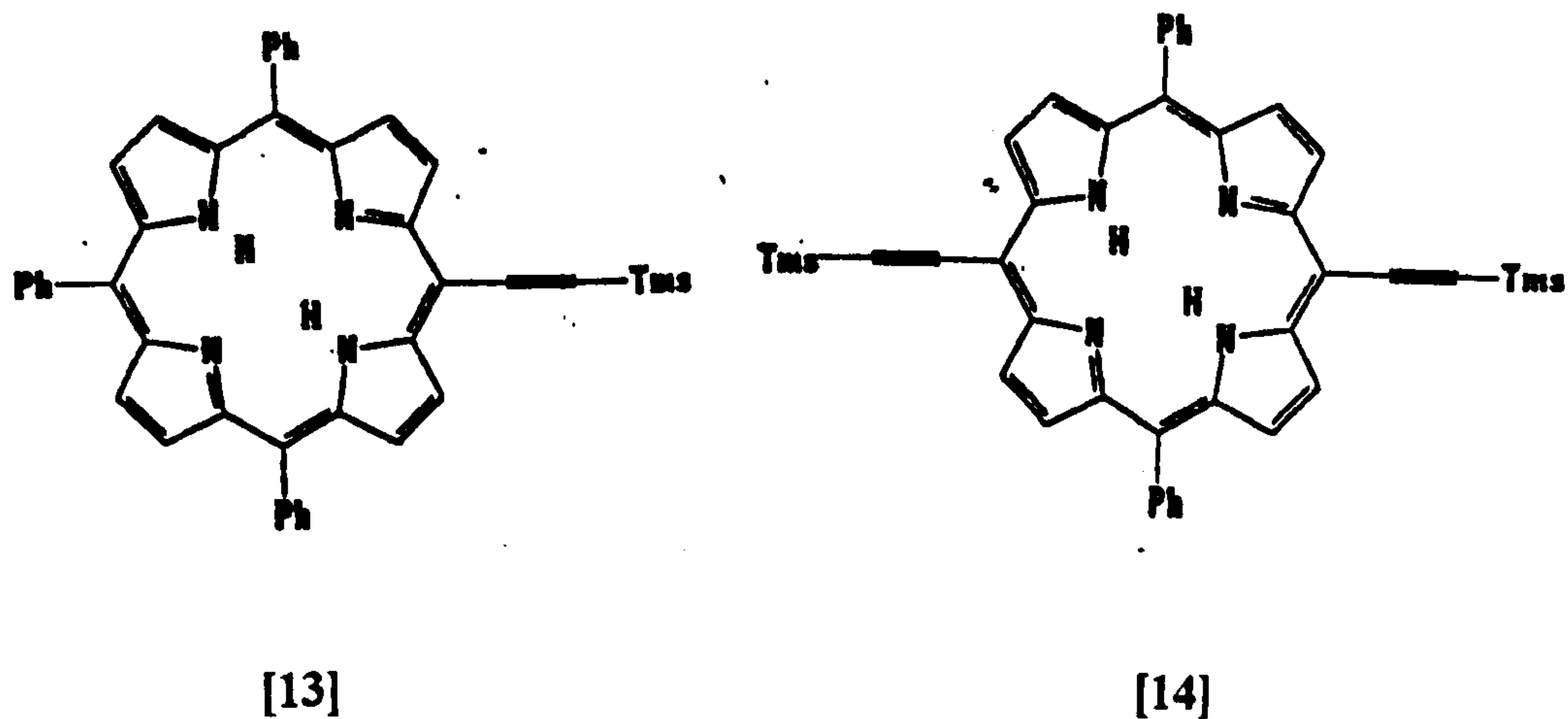


Figure 3.9

Porphyrin conjugation can be extended when the ethynyl group is linked to an aromatic entity other than a porphyrin. Therien synthesised a variety of asymmetrically-substituted [(5, 15-bisarylethynyl) -10,20-(diphenyl)] porphyrinato metal complexes. (Figure 3.10).

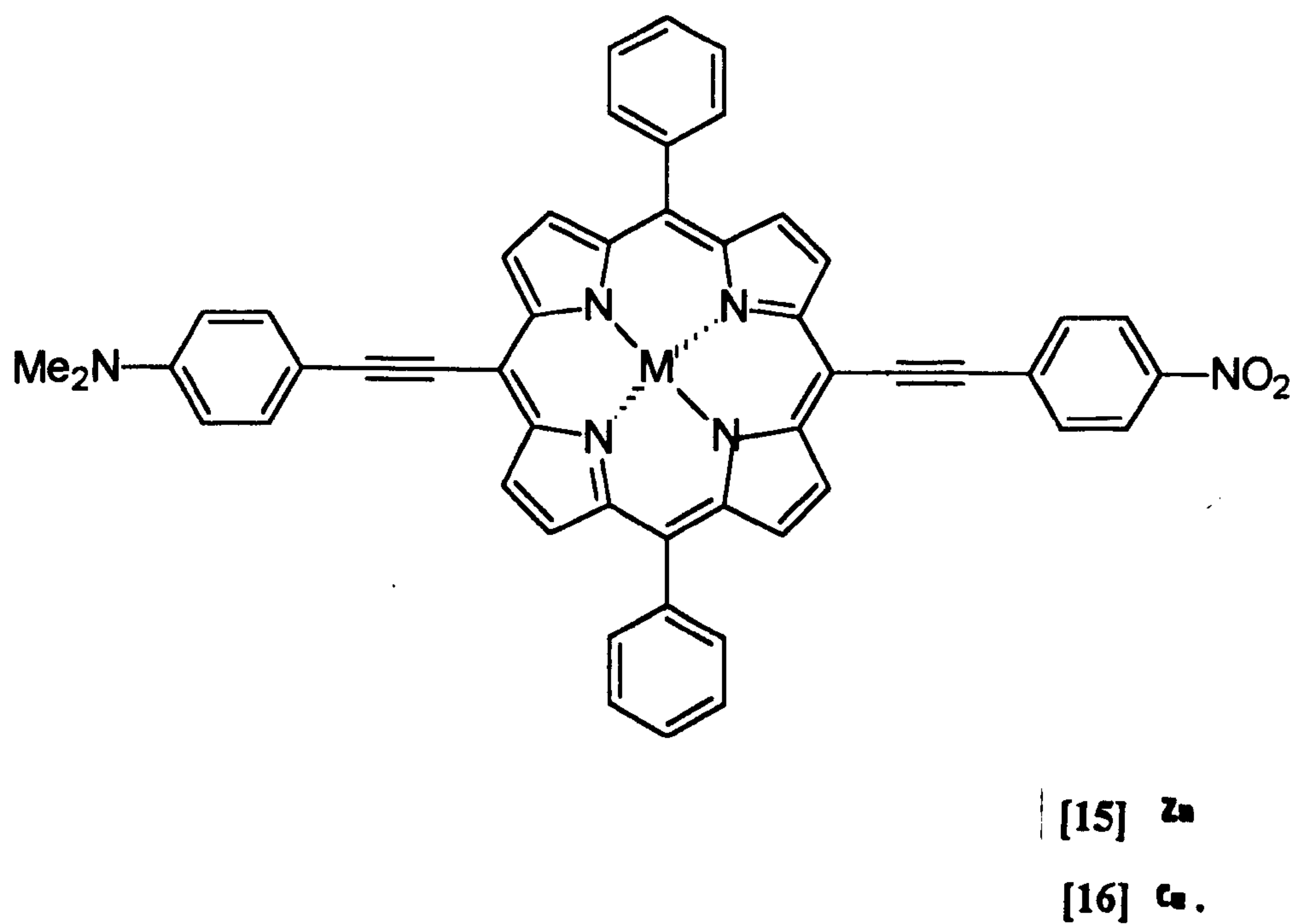


Figure 3.10

Measurements of the molecular first hyperpolarizability for the above compounds gave extremely large  $\beta$  values ( $\beta = 5000 \times 10^{-30}$  esu). This, in comparison with results from previous porphyrin arrays and other organic compounds (Table 3.1), indicates how exceptionally large the  $\beta$ -values are for the above mentioned compounds.

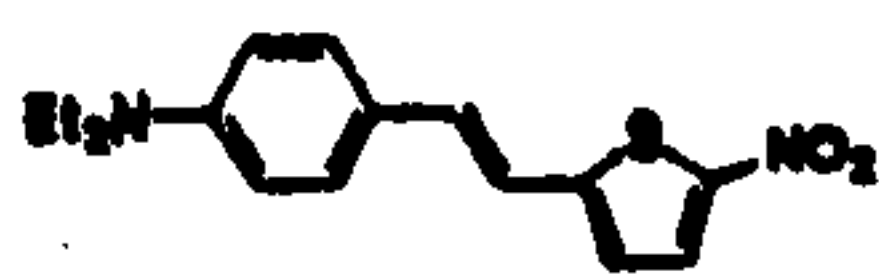
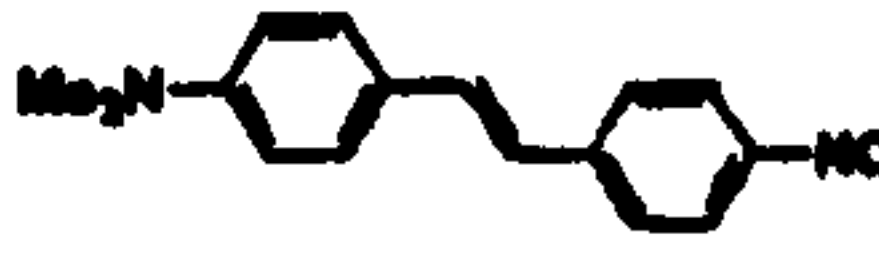
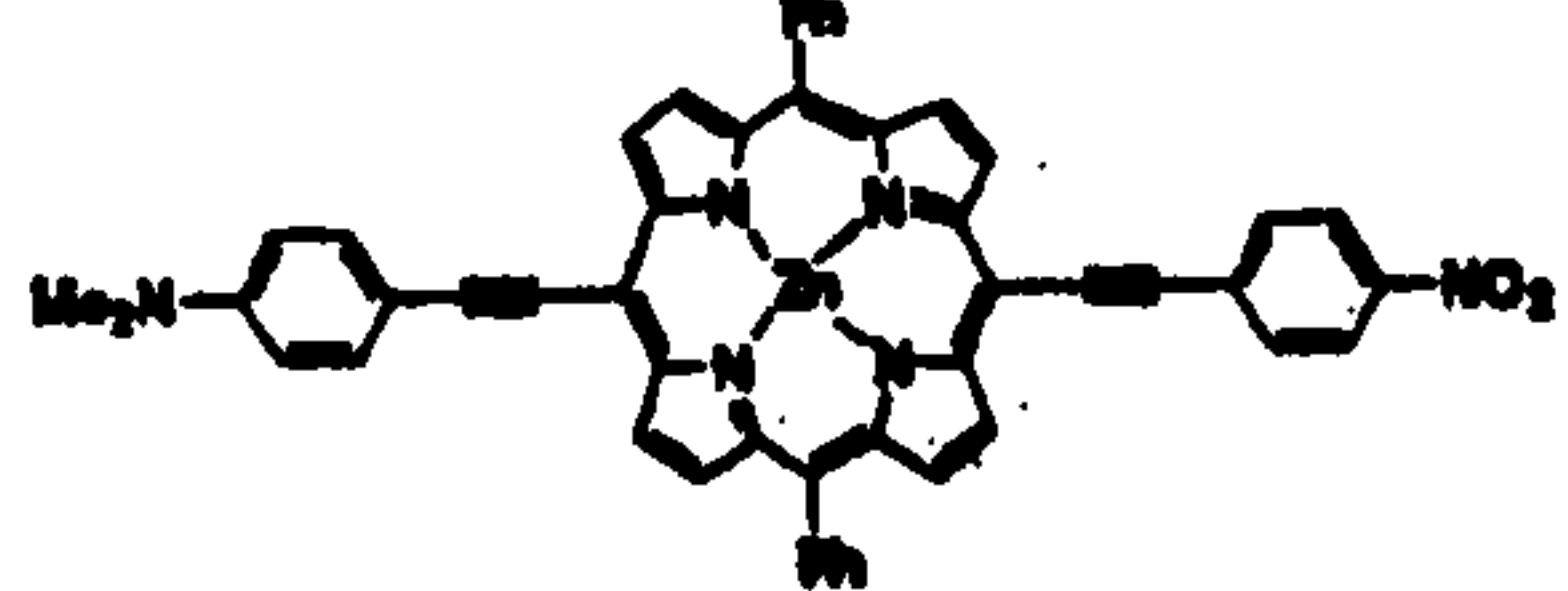
	$\beta_{(\lambda)}$	$\beta_{(0)}$	$\mu\beta_{(0)}$
			421
	73(1007)	55	363
	4833(1084)	900	9840

Table 3.1

This new class of compound along with those compounds yet to be designed, hold considerable promise for materials for second harmonic generation. It is evident that this system offers a number of advantages over the vast array of organic compounds that have employed the more typical unsaturable organic structures to bridge an electron donor and acceptor. The main reason why these compounds exhibit bigger  $\beta$ -values is the ease at which they align their large transition dipoles along the molecular charge transfer axis.

As already mentioned, porphyrins with their large polarizable  $\pi$ -electron systems and their wide choice of metal ions are attractive building blocks for third-order NLO materials. Porphyrin and its derivatives are found to exhibit large third order NLO susceptibilities.<sup>(39)</sup> Work carried out by Rao et al<sup>(39)</sup> on a series of benzoporphyrins in THF using the degenerate four wave mixing method have yielded results in the range  $1.2 \times 10^{-8}$  esu -  $2.8 \times 10^{-8}$  esu. Rao et al<sup>(39)</sup> also looked at the effect of substituents and how this affected the third-order nonlinearities. An attempt to correlate the effect of substituents with  $\chi^3$

for a series of tetrabenzoporphyrins possessing electron-donating as well as electron withdrawing substituents was carried out. The results indicate that compounds having strong electron donating substituents exhibit higher nonlinearity. However, as only preliminary research was carried out further studies are essential before any conclusions can be made.

Rao et al<sup>(50)</sup> then went on to look at how metal insertion affected the third-order nonlinearities by using two metallo derivatives of benzoporphyrins studied in his previous work.<sup>(39)</sup> There is a clear dependence observed with the metal substituent. From the observations it is evident that  $\chi^3$  values for unfilled d-shell ions are several times higher than those corresponding to H<sub>2</sub>Por and ZnPor. The results showed that the dependence of metal substitution followed a general trend: H<sub>2</sub>Por < ZnPor < CuPor < NiPor < CoPor, with the highest results obtained for cobalt. The enhancement of  $\chi^3$  can be associated with the contribution of additional electronic levels afforded by the introduction of a metal.

Shimizu et al<sup>(51)</sup> have studied the third-order nonlinearities of metallo phenylporphyrins. These studies are based on the 5,10,15,20-tetrakis (4-n-pentadecylphenyl) porphyrin and its metal complexes (Figure 3.11).

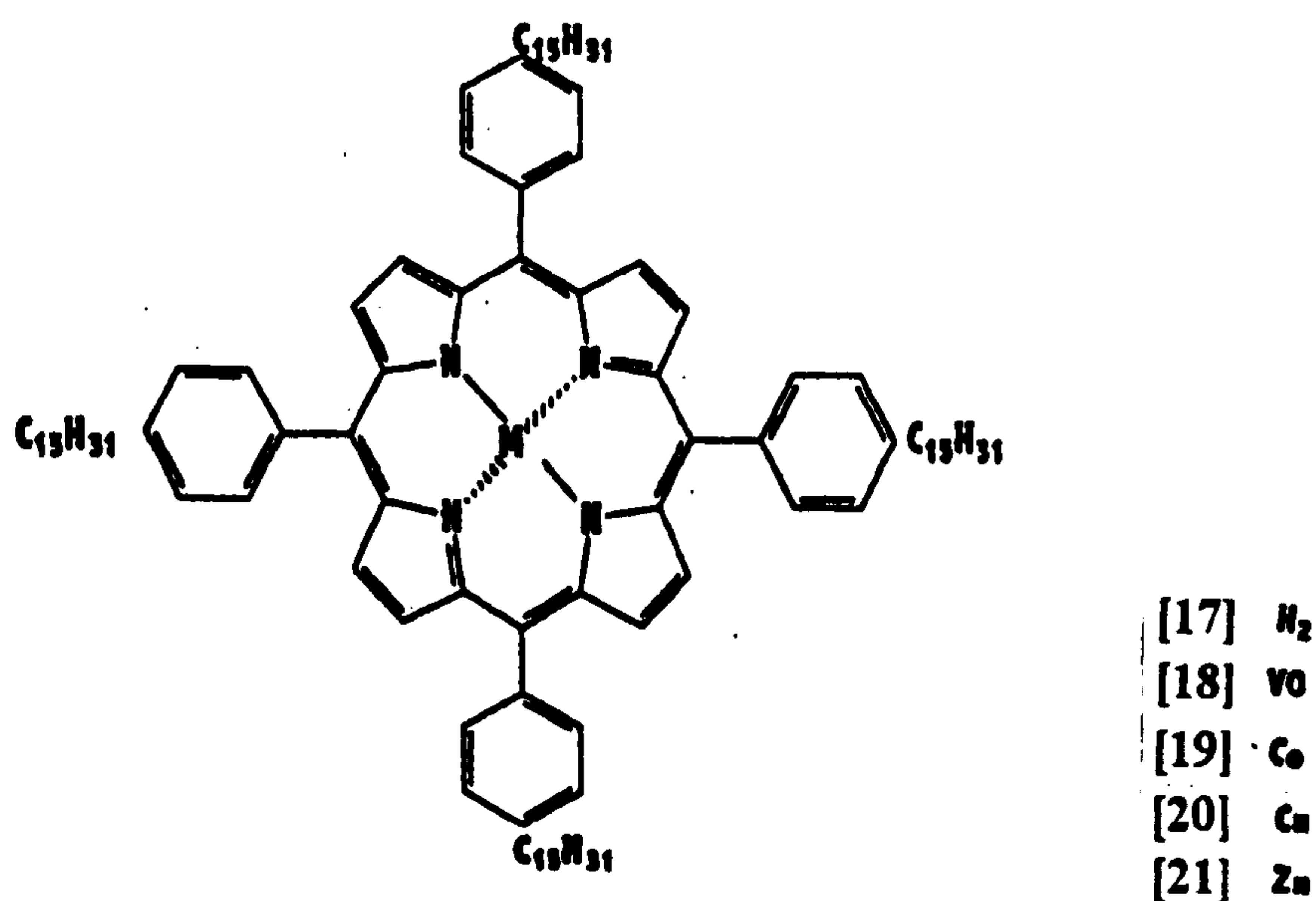
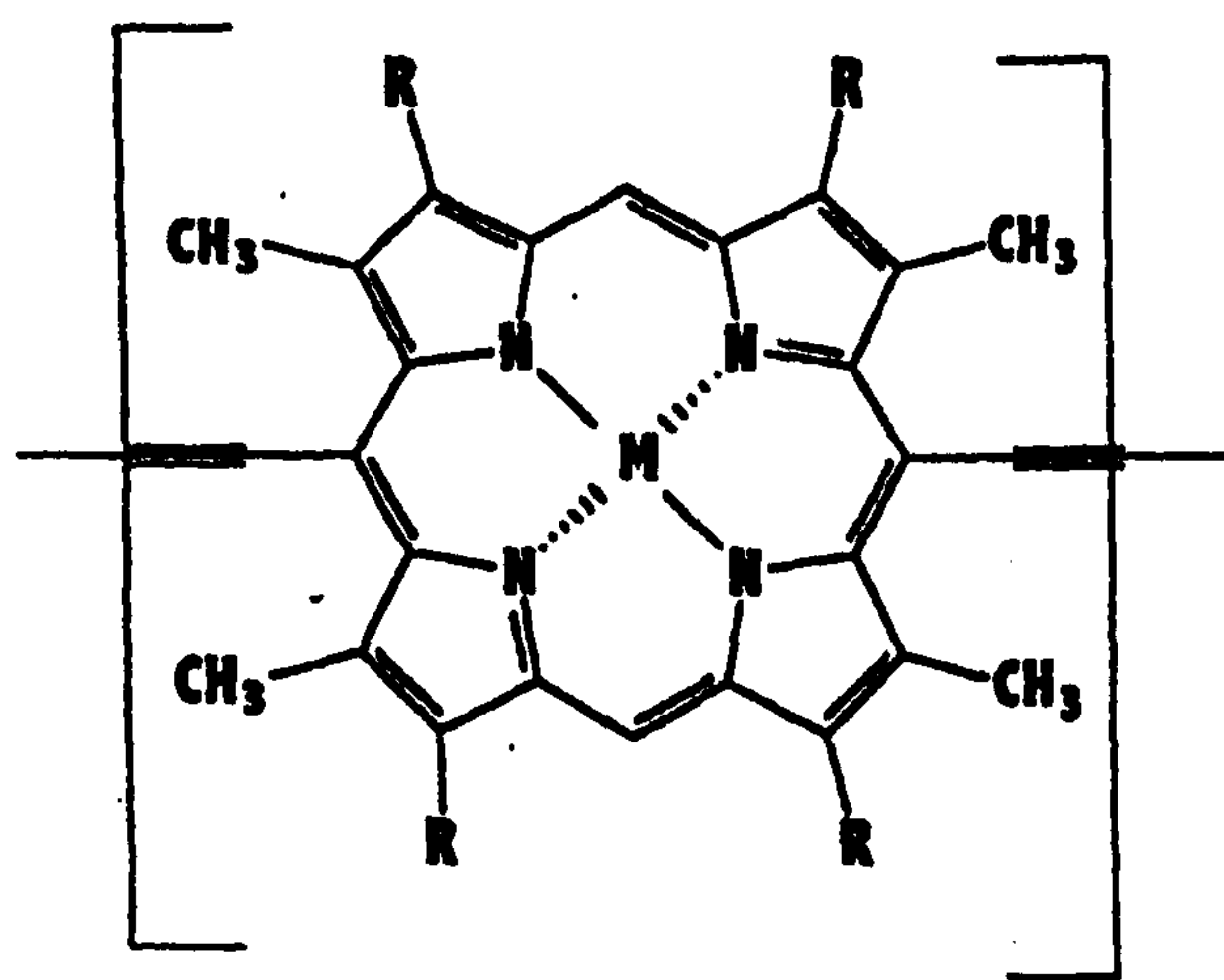


Figure 3.11



The  $\chi^3$  values obtained from the DFWM method were of the order of magnitude  $\approx 10^{-11}$  esu. These results are comparable with those of C. Maloney et al for metalloporphyrins without substituents.<sup>(52)</sup>

A conjugated polymer with porphyrin as the repeating unit should exhibit enhanced third-order NLO properties owing to its extended  $\pi$ -system. Anderson et al<sup>(53)</sup> reported the synthesis of a conjugated polymer [22] containing Zn-porphyrins linked with acetylene groups (Figure 3.12).



[22]

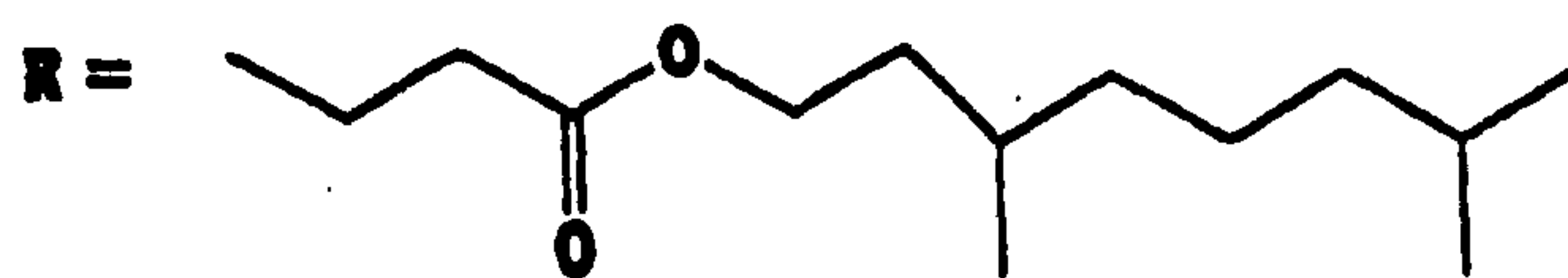


Figure 3.12

It was synthesised by Glazer-Huy coupling of the meso-diethynyl zinc porphyrin. The use of the ethynyl groups as spacers ensured that the conjugation could be extended throughout the system. The electronic structure was investigated by using electronic absorption spectroscopy. A dramatic red

shift and intensification of the Q band was observed due to the elongated conjugation length. Third-order nonlinearity tests on the polymer gave  $\chi^3$  values in the region  $7.3 \times 10^{-8}$  esu and this is comparable with most of the  $\pi$ -conjugated polymers such as polyacetylene ( $9.25 \times 10^{-8}$  esu).

From various reports presented, it is evident that the optical nonlinearity can be tuned by changing the central metal atom, peripheral substituents and ring size. The dependence of the optical nonlinearity on the extent of  $\pi$ -delocalization is also evident. Studies carried out on a series of basket-handle porphyrins<sup>(54)</sup> indicate that the third-order nonlinear susceptibility is decreased as the deformation in the porphyrin ring is increased. Thus, any steric hindrance and conformational disorder affects the  $\pi$ -electron delocalisation, which in turn affects the nonlinear optical behaviour of the two-dimensional systems.

The effects of reverse saturable absorption have been observed for tetraphenyl porphyrins<sup>(55)</sup> when dissolved in toluene and irradiated with 80 ps pulses at  $\lambda$ -532 nm. As already explained reverse saturable absorption occurs when the absorption cross-section from the excited state up to a higher excited state is larger than the absorption from the ground state to the excited state. The dyes investigated were tetraphenylporphyrins ( $H_2TPP$ ) < zinc (ZnTPP) and cobalt(CoTPP). The metal ion has a strong influence on the photophysical properties of the dye.<sup>(56)</sup> All three porphyrin systems exhibit reverse saturable absorption to some extent and this was easily adjusted by changing the central metal ion.

More recently reverse saturable absorption has been investigated in meso-substituted tetrabenzoporphyrins,<sup>(57)</sup> since the previous work showed results that were quite different. A series of metallobenzoporphyrins with different substitution patterns on the phenyl rings were tested, the metals being Zn, Cu, Ni and Pd. Several characteristic spectroscopic and kinetic features for the various metal-substituted tetrabenzoporphyrins were observed. ZnTPTBP exhibited both  $^1(\pi, \pi^*)$  and  $^3(\pi, \pi^*)$  transitions, while the heavy atom substituted

PdTPTBP and PdTMPTBP showed only  $^3(\pi,\pi^*)$  absorption. However, no large changes were observed between meso-p-methoxyphenyl and meso-phenyl derivatives.

The tetraphenyltetrabenzoporphyrins of Pd and Zn have also been incorporated into solid state inorganic matrices using the sol-gel process.

The sol-gel process is a technique where transparent matrices capable of hosting different types of organic and/or inorganic molecules are prepared.<sup>(38)</sup> The effect of incorporating the porphyrins into the xerogel samples affects the absorption spectra only slightly with additional weak absorption bands at 500 and 700 nm. This is most likely due to the partial demetallation, as suggested by Nomura et al.<sup>(59)</sup>

The overall stability of the doped xerogels indicates that the Zn complex is slightly less stable than its Pd counterpart. The results obtained from this experiment demonstrates that the tetraphenyltetrabenzoporphyrins can be conveniently incorporated into inorganic matrices using the low temperature sol-gel process and the resulting doped xerogels can act as effective optical limiters with low nonlinear activation thresholds.

Brunel et al<sup>(60)</sup> also carried out work with aluminophthalocyanine doped xerogels. Nonlinear reverse saturable absorption behaviour was observed for both nanosecond and picosecond pulse excitation at 532 nm.

In conclusion a considerable amount of effort has been spent in recent years trying to improve the nonlinear optic response and reverse saturable absorption properties of organic molecules. As demonstrated already, several breakthroughs have been achieved and a clearer outlook to improving the synthesis of nonlinear optical materials has been achieved.

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4 RESULTS AND DISCUSSION  
 PART 1. PORPHYRIN SYNTHESIS.

4.1 Synthesis of the Unsymmetrical 4-Pyridyl Porphyrin and its Derivatives

Porphyrins are well-known for their ability to be reduced and oxidised<sup>(1)</sup>. Consequently, the oxidation of 5,10,15,20-tetrakis-(3,5-di-t-butyl-4-hydroxyphenyl)porphyrin 23 has received a considerable degree of attention<sup>(2,3)</sup>. The introduction of the 4-pyridyl group to porphyrin 23 produces the unsymmetrical 5,10,15-tris-(3,5-di-t-butyl-4-hydroxyphenyl)-20-(4-pyridyl) porphyrin 24 and this provides a site for functionalisation and immobilization via quaternisation of the nitrogen group.

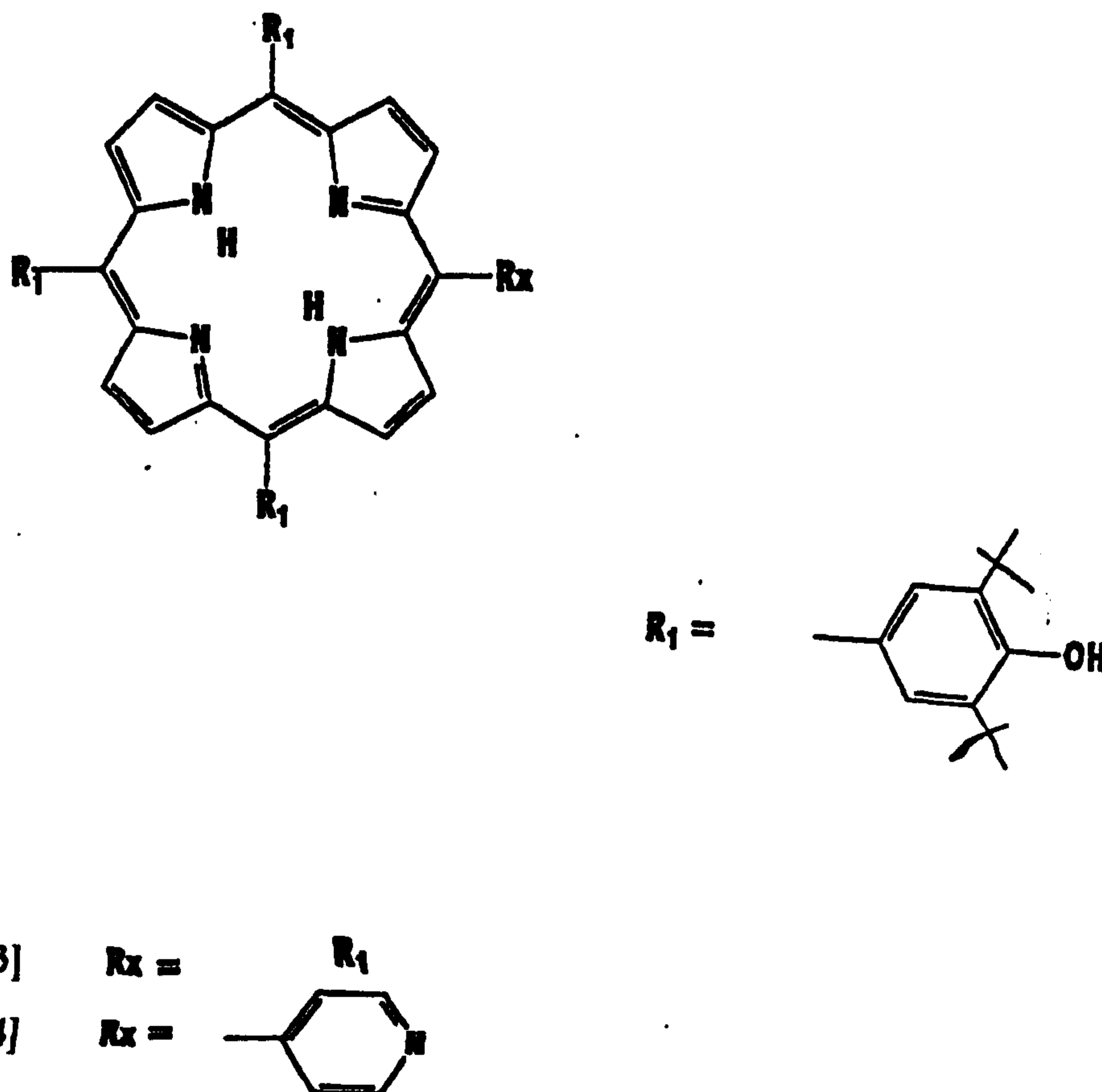


Figure 4.1. Structures of porphyrins 5,10,15,20-tetrakis-(3,5-di-t-butyl-4-hydroxyphenyl) porphyrin 23 and 5,10,15-tris-(3,5-di-t-butyl-4-hydroxyphenyl)-20-(4-pyridyl) porphyrin 24.



The introduction of the pyridyl group produces an unsymmetrical porphyrin and coupled with the porphyrin's ability to incorporate both electron donor and electron acceptor groups, produces systems that could exhibit second-order nonlinear optical activity. Subsequently, the synthesis of porphyrin 24 and a series of N-alkylations of the pyridyl nitrogen have been performed to produce porphyrins with different strength electron donor-acceptor groups and the second-order nonlinear optical activities investigated.

#### 4.1.1 **5,10,15-tris-(3,5-di-t-butyl-4-hydroxyphenyl)-20-(4-pyridyl) porphyrin**

Porphyrin 24<sup>(4)</sup> was synthesised by the Adler modification of the Rothmund procedure<sup>(5)</sup>. Thus, pyrrole was added to equimolar amounts of pyridine-4-carboxaldehyde and 3,5-di-t-butyl-4-hydroxybenzaldehyde and refluxed in propionic acid. The propionic acid was concentrated by distillation and the remaining acid taken off under reduced pressure. The residue was subsequently triturated with acetone to yield a mixture of porphyrins. This was subjected to column chromatography to yield the porphyrin as a purple amorphous powder (yield approximately 2.5%) which was in agreement with the literature method.

The mixed condensation of aldehydes with pyrrole produces a mixture of porphyrins and so column chromatography is essential to produce the desired porphyrin. Isolation of the porphyrin was confirmed by UV/visible spectroscopy, indicative of the characteristic free base porphyrin with a B band at 424 nm and the usual four Q bands. The NMR spectra of the monopyrindyl porphyrin 24 has an AB spin quartet for the pyrrole- $\beta$ -protons adjacent to these meso-substituents, observed previously in unsymmetrically meso-substituted porphyrins with electron-donating and withdrawing groups<sup>(6)</sup>.

## 4.2 N-Alkylation of 5,10,15-tris (3,5-di-t-butyl-4-hydroxyphenyl)-20-(4-pyridyl) porphyrin

The title porphyrin underwent a series of alkylations using a variety of different alkyl bromides (Table 4.1). The alkylations took place at the pyridyl nitrogen in an attempt to extend the porphyrin conjugation.


Table 4.1

### 4.2.1 N-Alkylation with benzylbromide

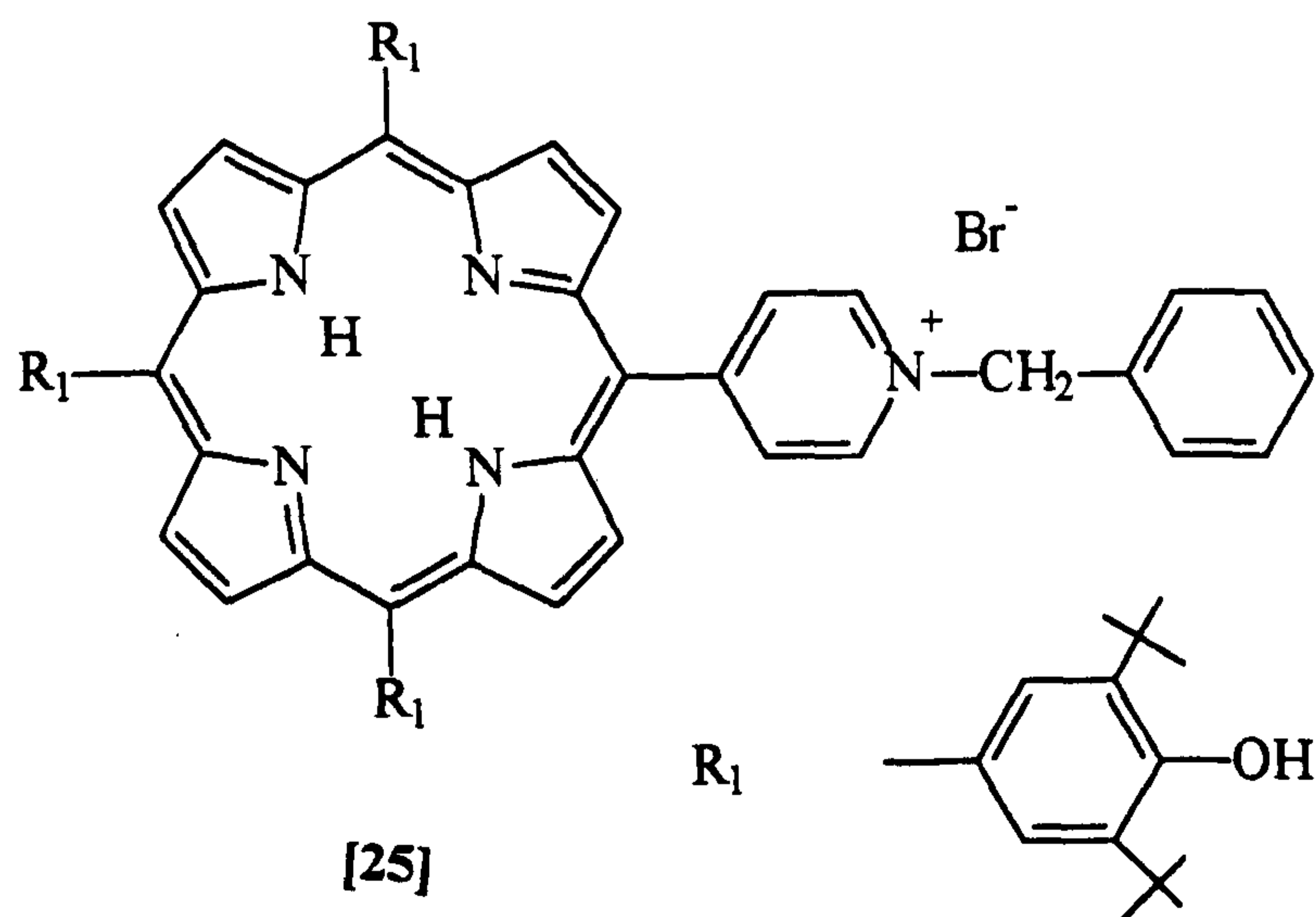


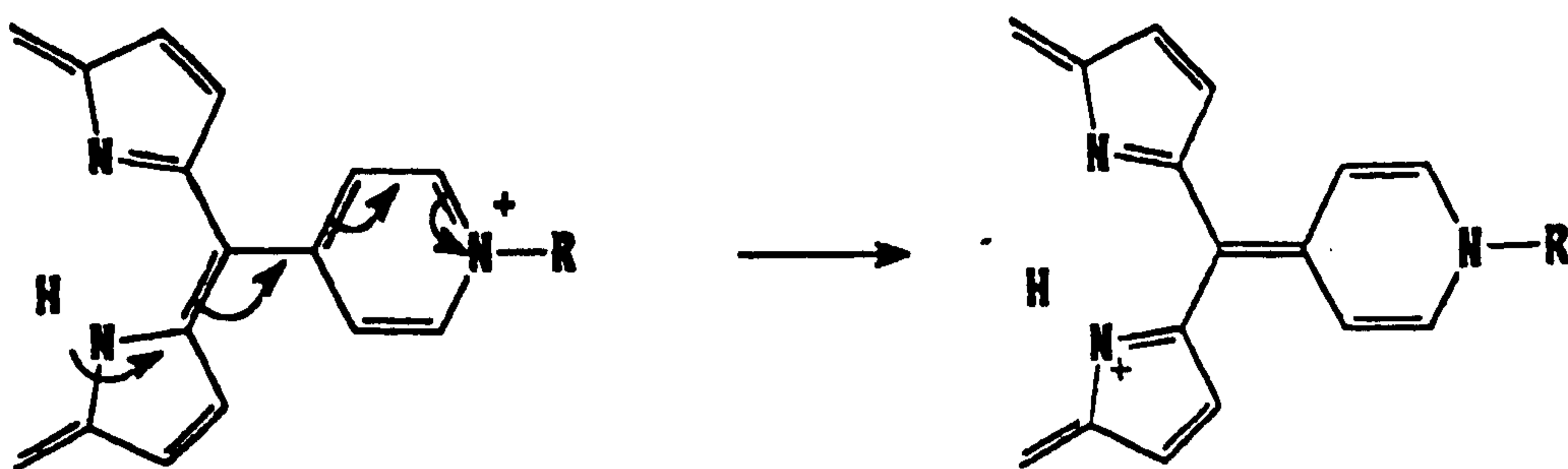
Figure 4.2

N-alkylation at the pyridyl position with benzyl bromide is carried out in an anomalous manner to the other reactions in this section. Unlike the standard alkylations where the porphyrin and alkylating agent are refluxed in a non-aqueous ionising solvent, the benzylation reaction has to be carried out in neat benzyl bromide. Milgrom et al <sup>(4)</sup> have previously reported that the benzylation via the standard route leads to alternative byproducts that have been isolated and characterised as the pentabenzylated oxidised porphyrin and the tribenzylated oxidised porphyrin.

The anomalous behaviour of the benzylation reaction can be explained by the formation of the relatively stable carbonium ion in the ionising solvent DMF enabling reactions of the S<sub>N</sub>1 and S<sub>N</sub>2 type. This is not encountered with the other alkylating agents we have employed due to the destabilisation effect on the carbonium ion by the electron withdrawing groups. This forces the reaction to proceed via the S<sub>N</sub>2 mechanism resulting in the formation of 4-pyridinium alkylated product as expected. The polybenzylated derivatives are produced by the reaction at the macrocycles central nitrogen atoms. The introduction of steric bulk into the area occupied by the central nitrogens is relieved by the buckling of the macrocycle, causing a lowering of the redox potential of the porphyrin to oxidation by the flow of electrons from the di-tert-butyl-4-hydroxyphenyl (DtBHP) groups onto the macrocycle<sup>(7)</sup>.

Benzylation of the unsymmetrical porphyrin in neat benzyl bromide resulted in the isolation of an amorphous purple powder and the NMR spectra of this compound confirmed that alkylation had occurred at the pyridyl position with the observed AB spin quartet for the β-pyrrole protons adjacent to the pyridyl group.

The uv/visible spectra for this compound 25 was unusual in that it only exhibits three Q bands and a B band of reduced intensity. Milgrom et al <sup>8</sup> suggest that the delocalisation of the pyridinium positive charge onto the macrocycle produces a resonance-stabilised monocation (Scheme 4.1) thus causing a three-Q-band visible spectra.



Scheme 4.1

This proposed mono-cation structure is somewhere between the porphyrin free-base which exhibits a strong B band and four Q bands and the porphyrin di-cation which exhibits weaker B bands and two Q bands.

#### 4.2.2 4-Nitrobenzylbromide

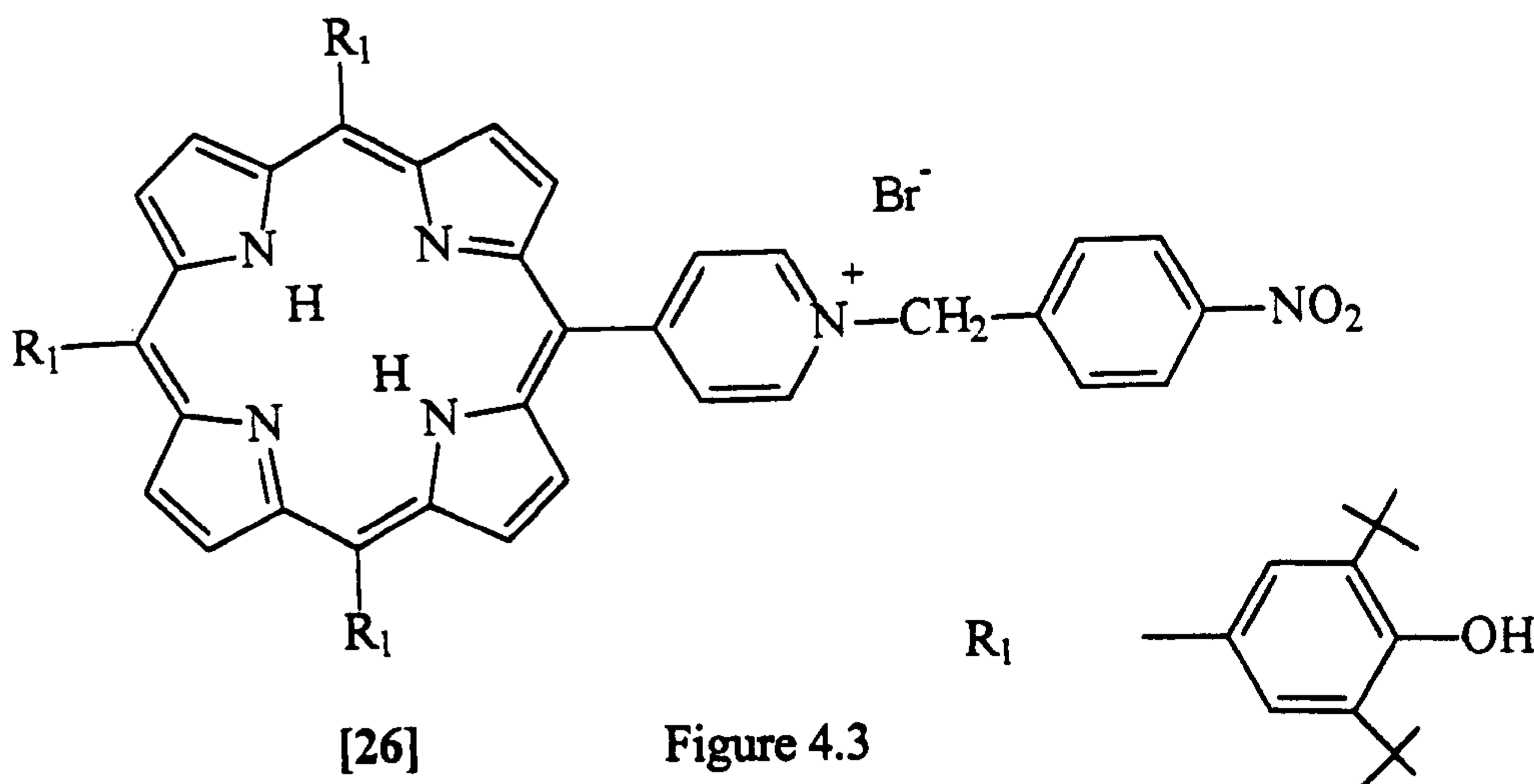


Figure 4.3

As previously mentioned the electron withdrawing 4-nitro group destabilises the 4-nitrobenzyl cation, thus forcing the reaction to proceed via the usual  $S_N2$  mechanism allowing the alkylation to be carried out in DMF. Removal of solvent and basic column chromatography yielded a purple amorphous powder which gave the similar characteristic NMR spectra and UV/visible spectra as the previously prepared benzylated porphyrin. Again, a three Q band and B band of reduced intensity is demonstrated indicative of the presence of a

porphyrin mono-cation. The inclusion of the nitro group to the benzyl ring induces only a minor change to the UV/visible spectra with a hypsochromic shift of the B and Q bands with the B band at 425 nm.

Attempts to oxidise porphyrin [26] were not carried out as this had already been investigated and this was not required for our purposes. The porphyrin does undergo oxidation in basified solution, but unlike the benzyl porphyrin [25] which gives a UV/visible spectrum similar to an oxidised porphyrin (i.e. with no B band, but broad red shifted bands), the nitrobenzyl porphyrin gives an intense band at 470 nm. This observation is explained as a direct result of the removal of a 4-nitrobenzylic-CH<sub>2</sub> proton generating a negative charge that can delocalise over the macrocycle and the 4-nitrobenzyl group<sup>(4)</sup>.

#### 4.2.3 $\alpha,\alpha'$ -Di-bromo-*p*-xylene

The N-alkylation of the pyridyl group with  $\alpha,\alpha'$ -di-bromo-*p*-xylene, like that of the 4-nitrobenzyl derivative, was carried out in a non-aqueous ionising solvent. The destabilising effect of the bromine group at the 4-position, again, prevented any stable carbonium ion formation. The choice of solvent was of greater importance due to the replacement of the bromine atoms by hydroxyl groups leading to a complex mixture of compounds. Initial N-alkylations in DMF proved unsuccessful as the bromine groups were rapidly hydrolysed producing a mixture that remained insoluble when column chromatography was performed. Attempts to isolate any characterisable compounds proved unsuccessful as the increase in polarity of the hydroxyl group required severe chromatographic conditions, thus not enabling the isolation of any pure compound.

The N-alkylation was carried out in sodium dried toluene in order to eliminate the problem of the bromine groups being hydrolysed. The first attempts to alkylate the porphyrin following the procedures described for the nitrobenzylation reaction produced a mixture of compounds, which upon

column chromatography, could be easily separated to give characterisable compounds.

Two products were isolated and the UV/visible spectra for both compounds were consistent with the UV/visible spectra for the benzyl and 4-nitrobenzyl alkylated porphyrins. The bathochromic shift of the B band, experienced for the others, coupled with the noticeable broadening of the B band and the relatively high intensity of the Q bands indicated the mono-cation formation associated with the previous N-alkylates.

The two products isolated consisted of one in which one of the bromo groups reacted [27], and the other in which both the bromo groups reacted to give a dimer[28].

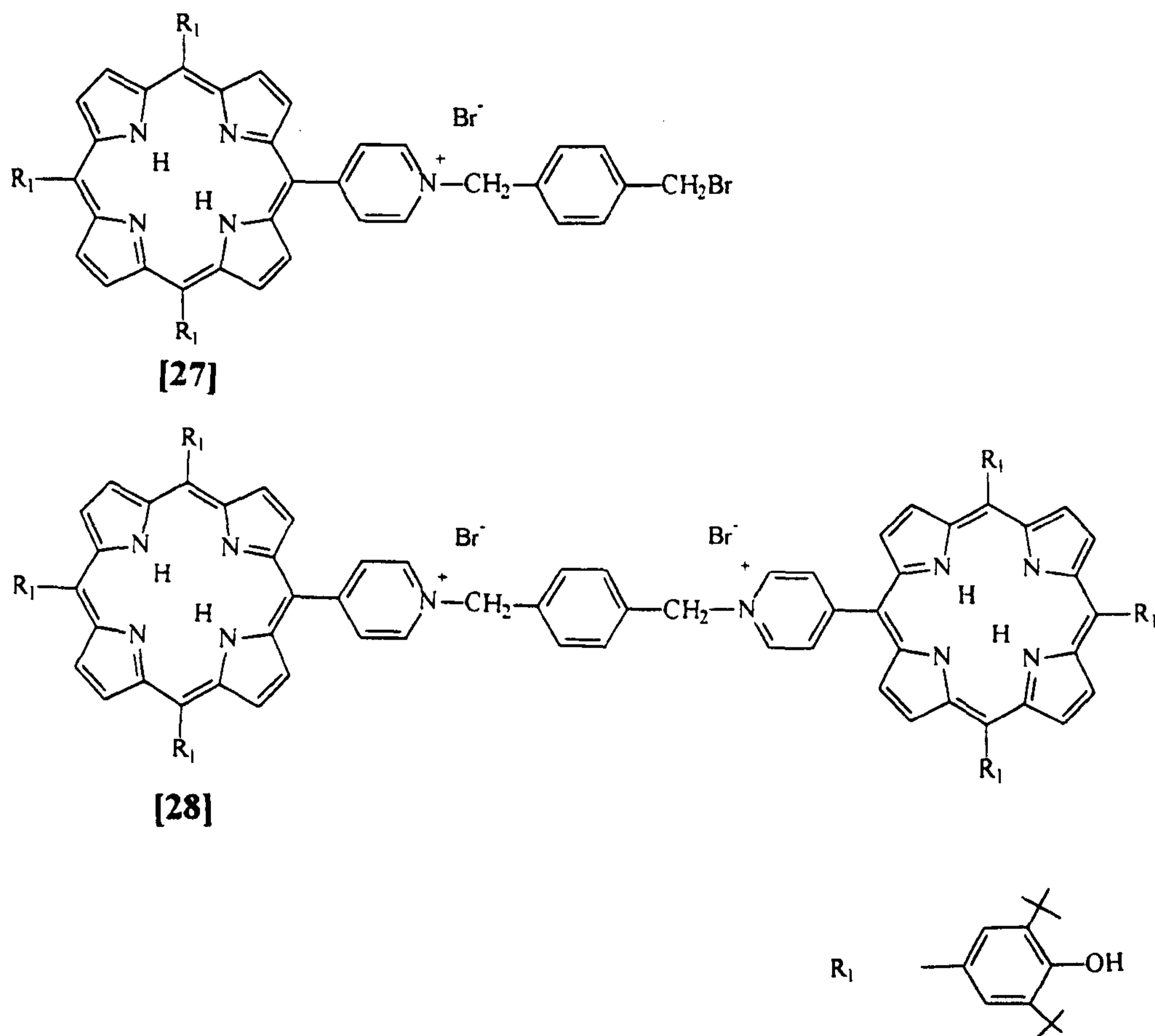


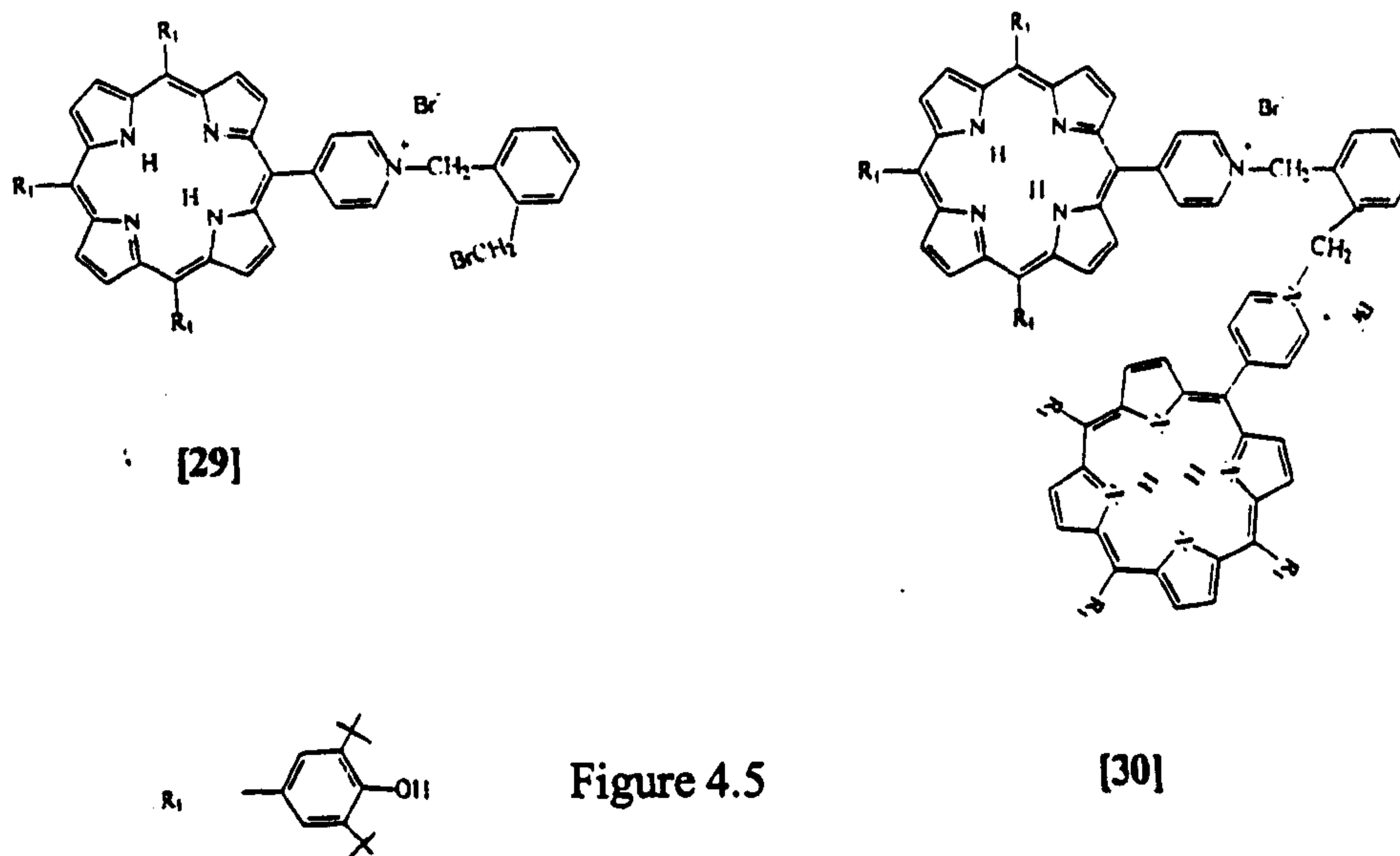
Figure 4.4

Inspection of the nmr spectra of both compounds confirms the proposed structures due to the fact porphyrin [27] has two  $-CH_2-$  resonances and porphyrin [28] only has one. In the dimeric structure, the  $-CH_2-$  resonances are in an identical environment, and hence, appear as a singlet with the loss of the  $-CH_2Br$  peak at 4.35 ppm. The fact no other resonance peaks appear confirms the fact the  $-CH_2$  protons are in the same environment and that hydrolysis hasn't occurred.

Manipulation of reaction conditions such as solvent volume and the stoichiometry of reactants can be utilised to synthesise one form over the other. The dimeric form is favoured when the solvent volume is reduced and the ratio of  $\alpha,\alpha'$ -di-bromo-*p*-xylene lowered in comparison to the porphyrin. The reduction of solvent volume ensures that the probability of the porphyrin reacting with the same molecule of  $\alpha,\alpha'$ -Di-bromo-*p*-xylene is increased and lowering the concentration of the alkylating agent also has this effect.

#### 4.2.4 $\alpha,\alpha'$ -Di-bromo-*o*-xylene

The alkylation with  $\alpha,\alpha'$ -di-bromo-*o*-xylene was carried out under identical conditions to the para derivative. Again, two compounds were identified from initial TLC observations.



The resulting mixture needed careful separation on a silica gel column using a 50:50 mixture of chloroform/ acetonitrile as the eluent. However, employing this system, was only efficient in separating the dimeric product [30] from the mixture as [29] contained some contaminant. Attempts were made with several eluting mixtures on a range of different packing materials to purify [29], but these all proved unsuccessful. Inclusion of different metal ions into the macrocycles centre were performed before alkylation, in an attempt for easier separation, but again only the dimeric product was isolated pure.

The dimer was eluted from the column as a purple powder with a yield approximately 40% and UV/visible spectroscopy of this compound was similar to the previously mentioned N-alkylates with the characteristic B band of reduced intensity and the three Q bands. The NMR spectra of the ortho dimer is different from that of the para derivative. Steric considerations have to be taken into account in the ortho form due to the closeness of the porphyrin macrocycles. The porphyrin contains DtBHP ortho-H in two environments but in the previous N-alkylates, including the para derivative, they only appear as a single resonance as the two environments are very similar. In the ortho derivative, the steric constraint induced by the closeness of the macrocycles, causes these resonances to split into two peaks in the intensity ratio 2:1.

Closer inspection of the UV/visible spectra of the dimer compounds [28, 30] confirm that conjugation was not established between the porphyrins. Increased conjugation on formation of the dimer would be complemented by a considerable red shift in the UV/visible spectrum but this is not experienced in either of the dimers synthesised. The electronic spectra of the dimers are consistent with those of the other alkylated porphyrins with the B bands within 4-5 nm of each other, showing that there is no conjugation from porphyrin to porphyrin. This is to be expected as the conjugation will be lost through the benzylic-CH<sub>2</sub>-bond. Ideally, for improved second-order nonlinear optical



materials, increased conjugation through the system is essential and this could be achieved by the introduction of ethynyl groups.

The NMR spectrum also suggests that the porphyrins cannot communicate with each other because there were no significant changes in the resonances of the porphyrin protons.

Increased conjugation from one porphyrin to the other would cause significant changes to the proton resonances encouraging them to shift downfield. As indicated by the NMR spectra of all the N-alkylated porphyrins, the proton resonances are almost identical confirming that the peripheral substitution is having little effect on the porphyrin protons.

#### **4.3 Metallations of the N-alkylated Porphyrins**

A series of metallations were carried out on the porphyrin N-alkylates, using literature methods for metal insertions <sup>(9)</sup>. Manganese was inserted into a number of the previously prepared porphyrins [24], [25], [26], and [27]. The metal ion in synthetic manganese porphyrins can exist in a large number of oxidation states and is therefore of particular interest to chemical reactivity and catalytic properties of the compounds <sup>(10)</sup>. A refluxing mixture of manganese chloride in dimethylformamide was treated with the individual porphyrin N-alkylate and the reaction followed by UV/visible spectroscopy. The reaction was complete when the four-banded visible spectrum of the free-base porphyrin was replaced by the two-banded visible spectrum of the metalloporphyrin (Table 4.2). The metal porphyrins were isolated by column chromatography and recrystallised as green solids from chloroform/hexane.

Porphyrin	$\lambda_{max}/nm$	% Yield
31	382.5, 408.5 482.0 589.5 628.0	88
32	374.5 485.0 590.0 633.0	68
33	375.5 485.0 591.5 635.0	74
34	374.5 485.5 592.0 634.0	53

[31] - Meso-5,10,15-tris-(3,5-di-t-butyl-4-hydroxyphenyl)-20-(4-pyridyl) porphyrinatomanganese.

[32] - Meso-5,10,15-tris-(3,5-di-t-butyl-4-hydroxyphenyl)-20-(4-{benzyl}pyridiniumyl) porphyrinatomanganese.

[33] - Meso-5,10,15-tris-(3,5-di-t-butyl-4-hydroxyphenyl)-20-(4-{4-nitrophenyl}pyridiniumyl) porphyrinatomanganese.

[34] - Meso-5,10,15-tris-(3,5-di-t-butyl-4-hydroxyphenyl)-20-(4-{4-bromomethylbenzyl}pyridiniumyl) porphyrinatomanganese.

Table 4.2

As already mentioned, a series of metals were inserted into the macrocycle centre of the ortho reaction mixture, in order to achieve a better separation. The metals inserted were Zn, Co, Mn and were inserted as directed by the literature method for metal insertion <sup>(9)</sup>. Introduction of the metals into the porphyrin's centre was monitored by UV/visible spectroscopy as previously described. The porphyrin mixtures were purified by column chromatography and then subjected to N-alkylation under the identical conditions to those of the free base porphyrins. Unfortunately, the attempts to separate the porphyrin mixtures proved unsuccessful as before, but the dimers were separated in good yields. The UV/visible spectra of these porphyrins are shown in Table 4.3.

Porphyrin	$\lambda_{\text{max}}/\text{nm}$			% Yield
35	434	502.5	634.5	83
36	438.5	555.0	599.5	77
37	381.5	489.5	592	63

[35] - Zn dimer (ortho)

[36] - Co dimer (ortho)

[37] - Mn dimer (ortho).

Table 4.3

#### 4.4 N-alkylation of Porphyrins and Porphyrinogens

The first attempt to directly alkylate the central nitrogens of the porphyrin macrocycle was reported by McEwen <sup>(11)</sup> with the mono-N-methylated etioporphyrins I and II and methyl iodide. McEwan also isolated the dimethylated product in reasonable yield, alkylating at N<sub>21</sub>, N<sub>22</sub> as indicated by proton NMR data. Tri-N-methylated porphyrins have been obtained with the stronger methylating agents, methylfluorosulphonate <sup>(12)</sup>, but these are somewhat unstable and proceeded to decompose to the N<sub>21</sub>, N<sub>22</sub>-dimethyl derivative upon chromatography. The N<sub>21</sub>, N<sub>22</sub>, N<sub>23</sub>, N<sub>24</sub>-tetramethyl porphyrins are inaccessible by direct methylation and attempts to synthesise them via the oxidation of the relevant tetra-methylporphyrinogen have been made<sup>(13)</sup>. These attempts proved unsuccessful due mainly to the steric crowding by the methyl groups present in the tetra-N-methylated porphyrinogen. N-Methylation of tetraphenylporphyrin has been attempted by the treatment with methyl iodide or methylfluorosulphonate, but like the previous work, only the mono-, di- and tri-N-methylated derivatives were formed.

However, tetra-N-methylation (Figure 4.6b) has been achieved on the porphyrinogens, octaethyl meso-tetramethylene porphyrinogen (Figure 4.6b) by

Breitmaier <sup>(14)</sup> and the octaethylxanthoporphyrinogen (Figure 4.6a) by Inhoffen et al <sup>(15)</sup>.

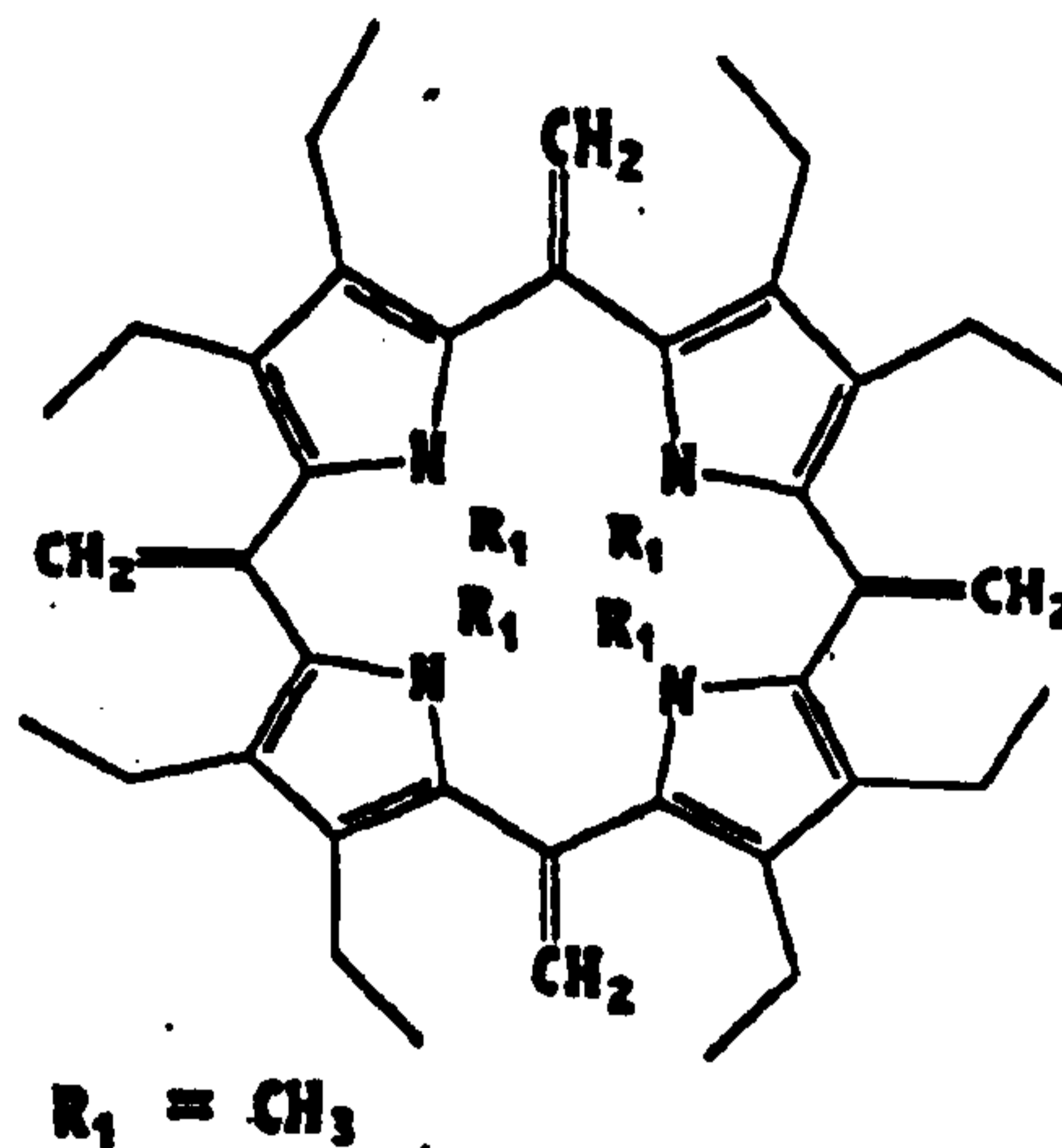
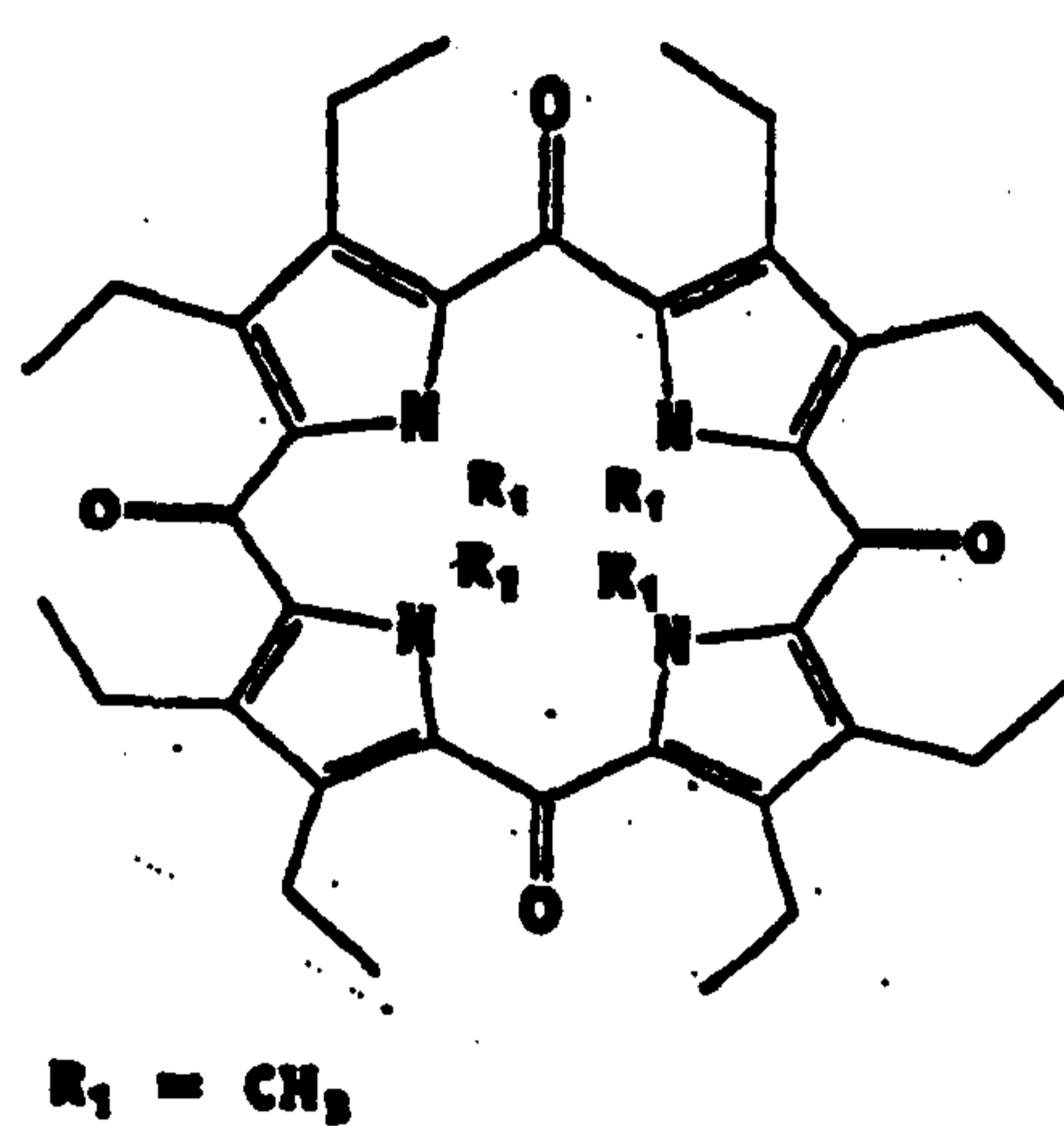
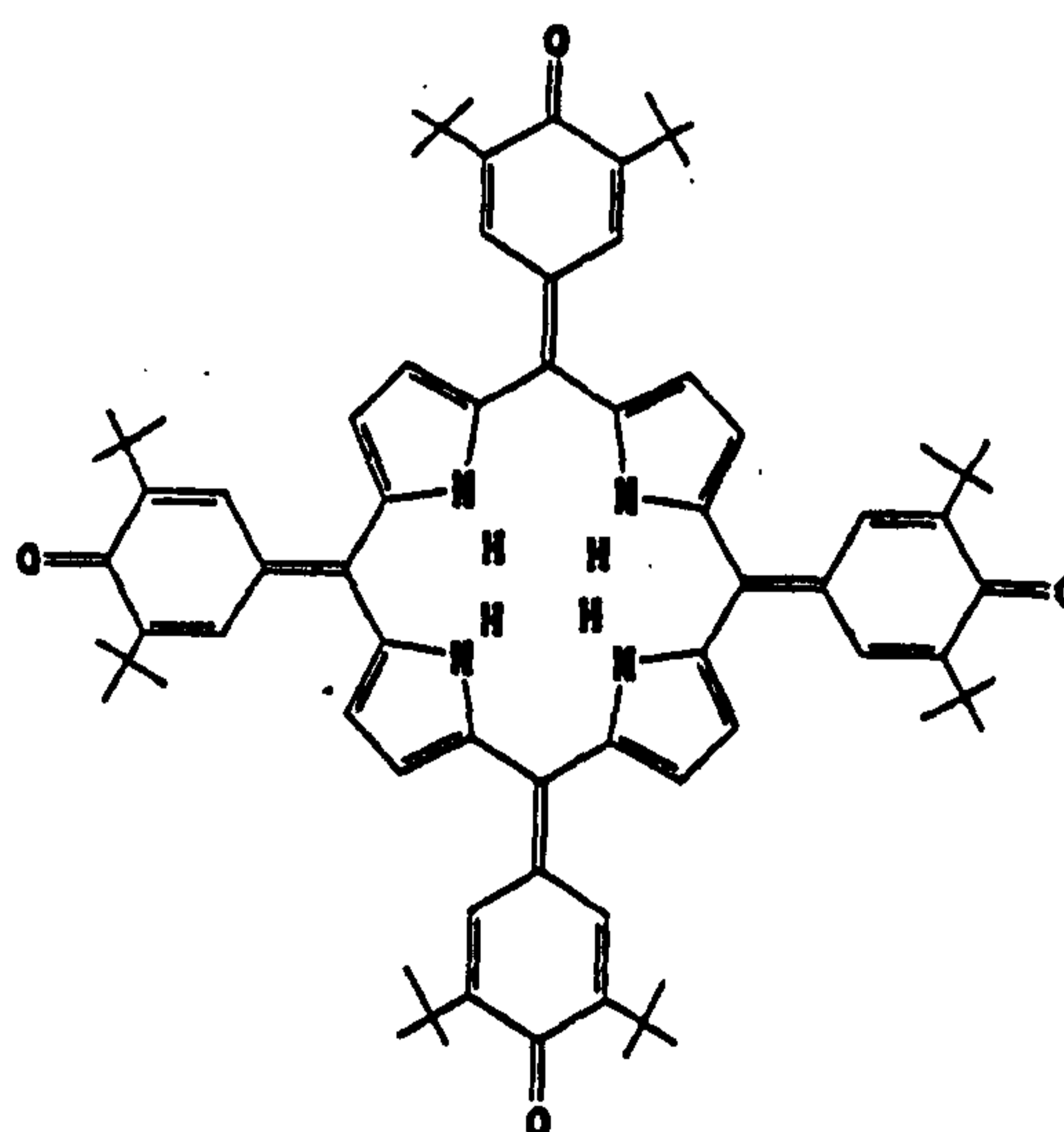


Figure 4.6a

Figure 4.6b

Of greater importance to this work is the structural analog meso-tetra-5,10,15,20-(3,5-di-t-butyl-4-oxacyclohexa-2,5-dienylene)porphyrinogen [38] Ox[T(DtBHP)P] (Figure 4.7) formed as a direct result of a facile two-electron oxidation of the parent porphyrin in basic solutions.



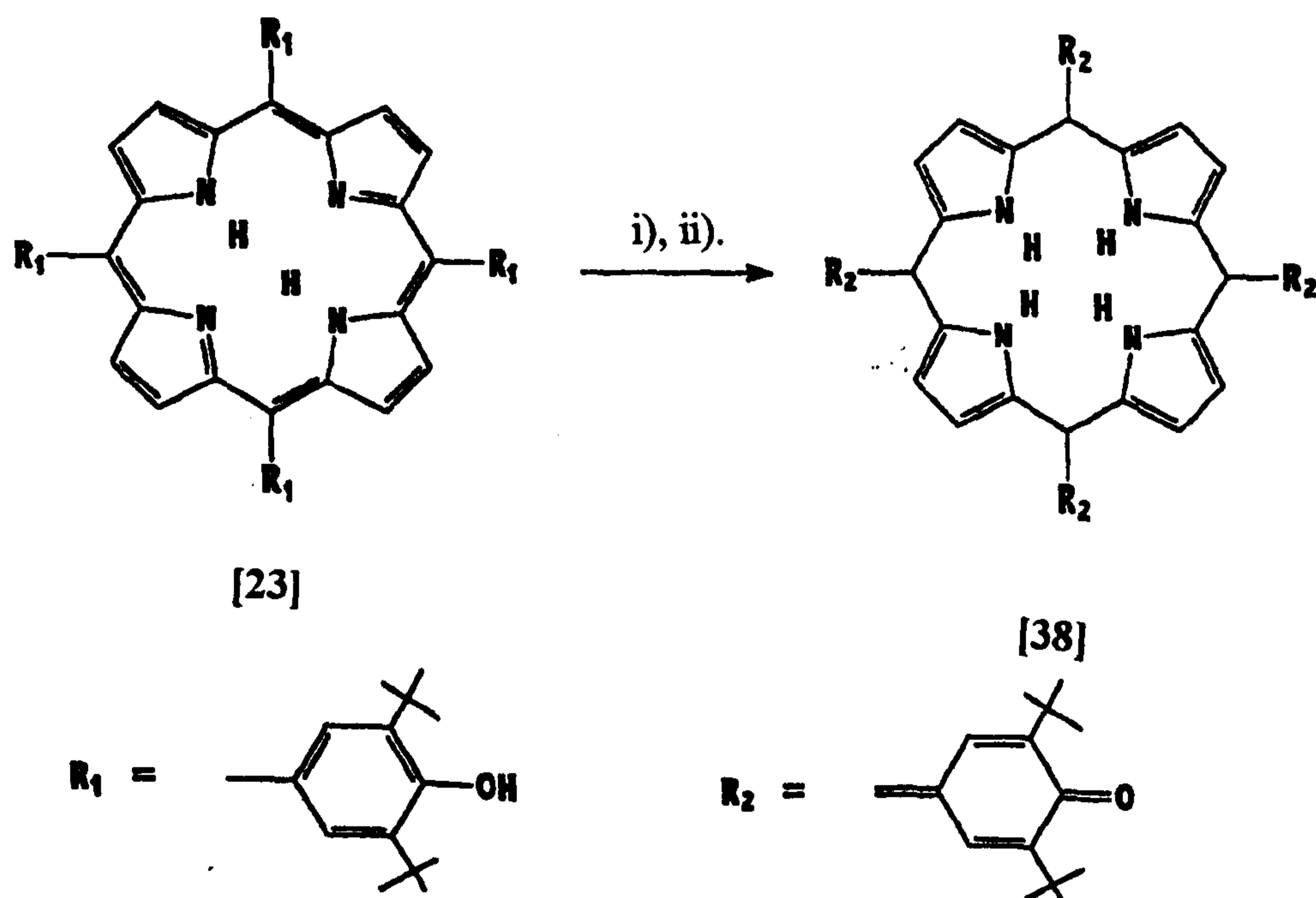
[38]

Figure 4.7 Ox[T(DtBHP)P]

This macrocycle is of particular interest as it is severely puckered <sup>(16)</sup> therefore providing possible sites for N-alkylation with alkyl and aryl halides. Milgrom et al <sup>(17)</sup> carried out a series of N-alkylations on the Ox[T(DtBHP)P] to produce a mixture of di- and tetra-N-alkylates with various alkyl and aryl substituents. Selectivity and yields for these reactions were poor with the di-N-alkyl derivative synthesised in higher yield. The aim of this work is to improve the selectivity and yields of the N-alkylates and perform nonlinear optical analysis on the N-alkylated products to determine their potential as nonlinear optical devices.

#### 4.4.1 Oxidation of meso-tetra-(3,5-di-t-butyl-4-hydroxyphenyl)porphyrin

The product obtained from the oxidation of meso-tetrakis (3,5-di-t-butyl-4-hydroxyphenyl) porphyrin has received particular attention since its discovery in 1983 <sup>(18)</sup>. The oxidation of the parent porphyrin 23 under basic conditions leads to the highly puckered oxidised derivative 38 (Scheme 4.2).



i) Methanolic KOH, CHCl<sub>3</sub>, 24Hrs, ii) TFA, H<sub>2</sub>O extraction.

Scheme 4.2

Initial attempts to alkylate the macrocyclic nitrogens by refluxing with an alkyl bromide in DMF, proved unsuccessful. Addition of a base to the oxidised porphyrin followed by the alkylating agent led to a mixture of N-alkylates.

In the solid state, the oxidised porphyrin exists as the highly puckered meso-tetrakis(3,5-di-t-butyl-4-oxacyclohexa-2,5-dienylene)-porphyrinogen **38** <sup>(18)</sup>. X-ray diffraction analysis of crystals grown from solution of the oxidised porphyrins confirm this extraordinary puckering of the macrocycle <sup>(16)</sup>.

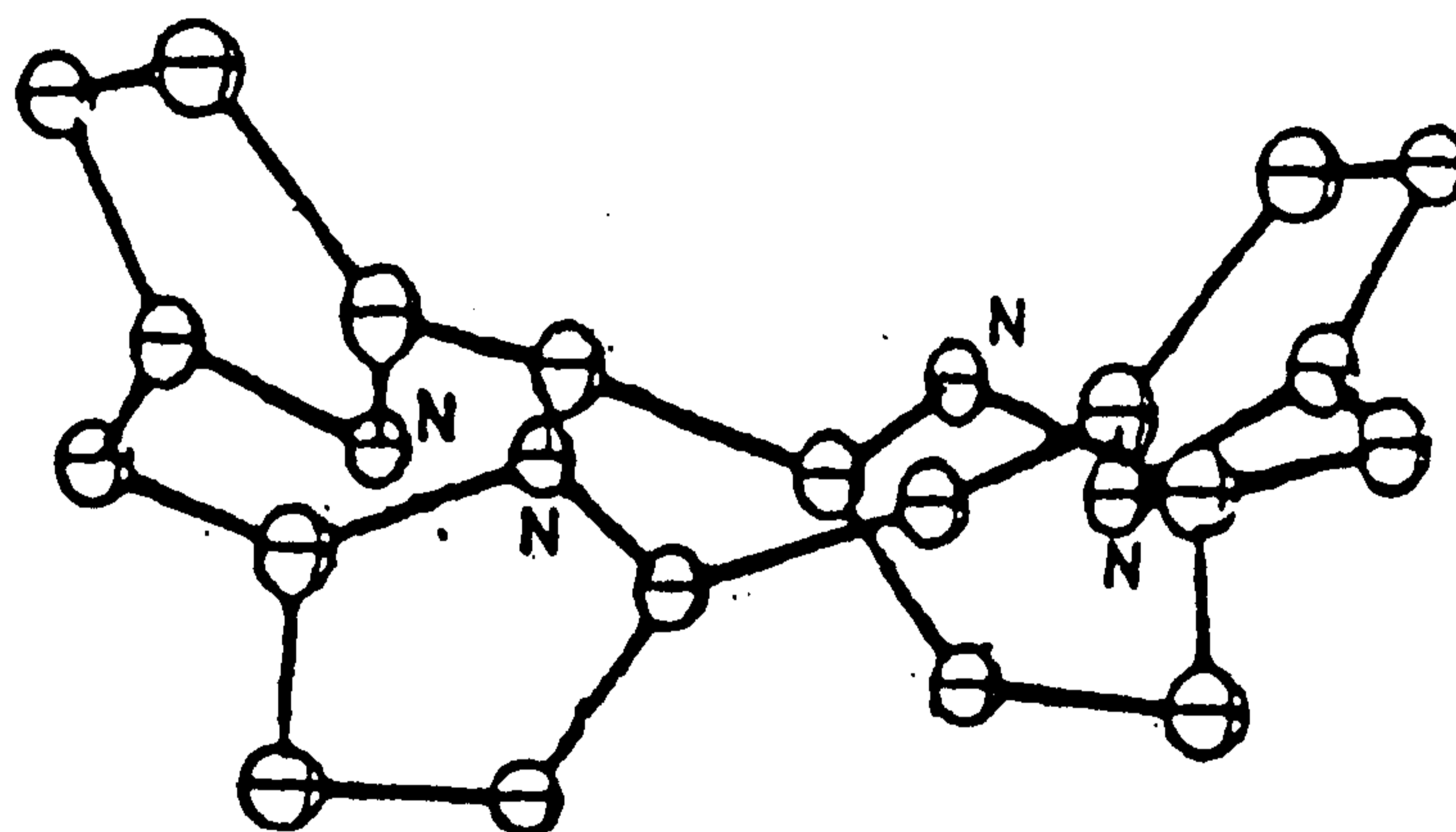
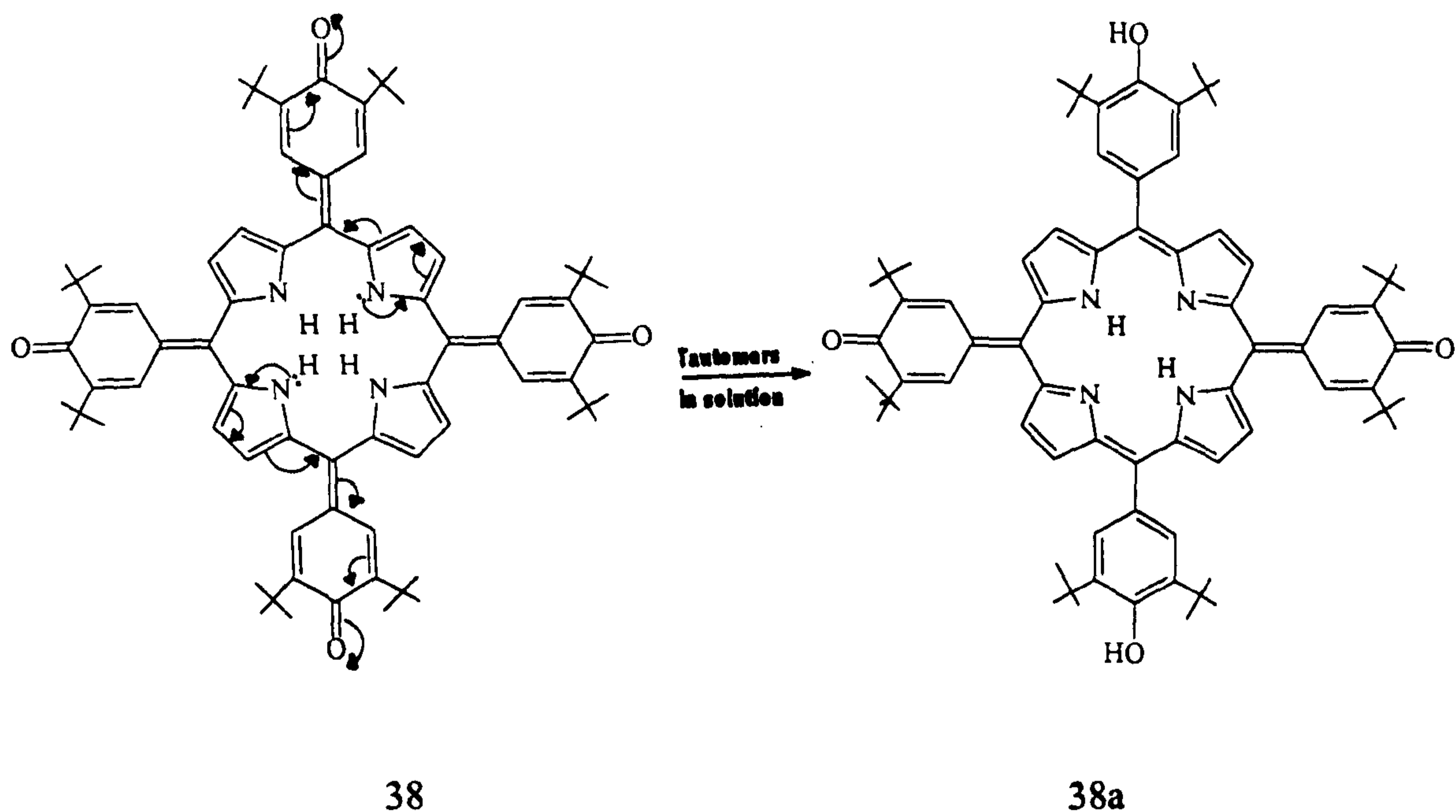


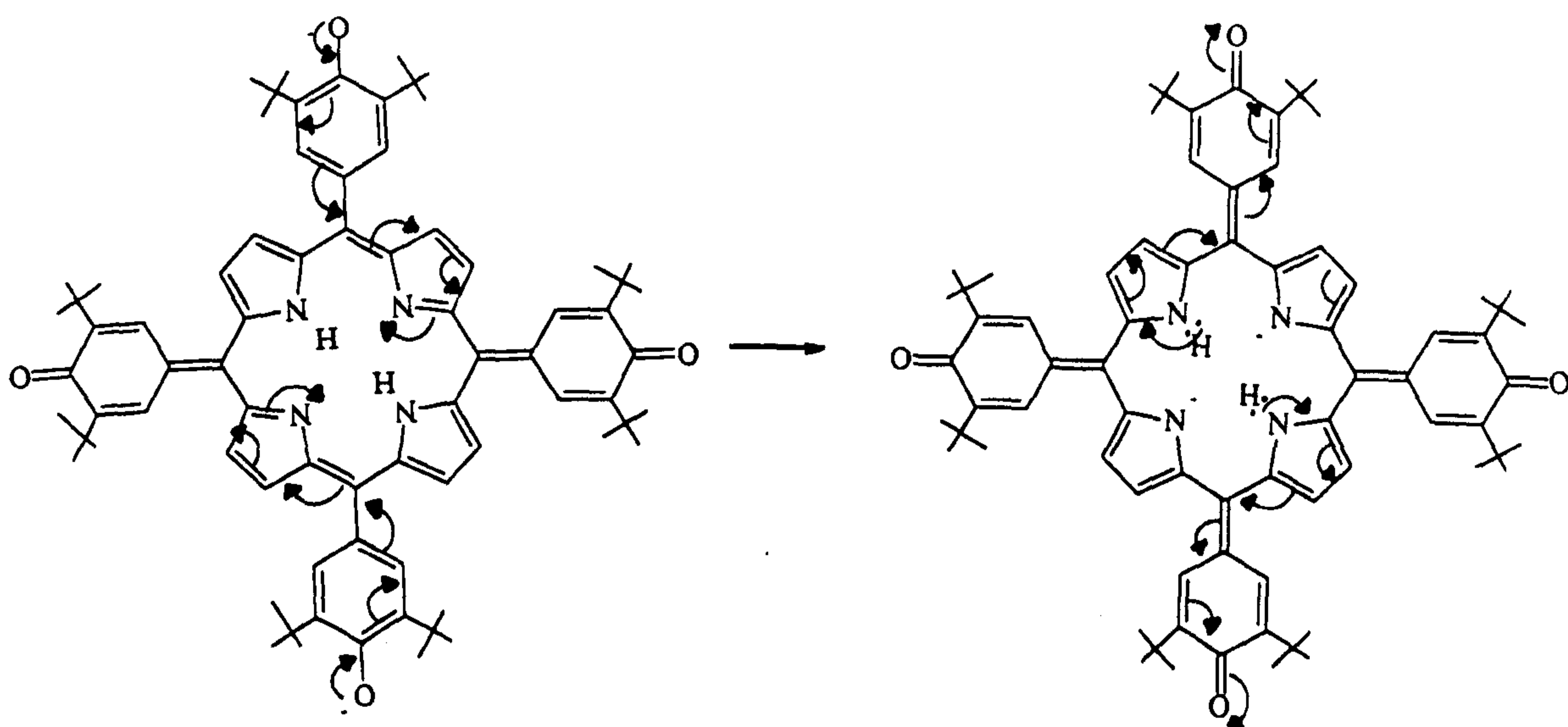
Figure 4.8

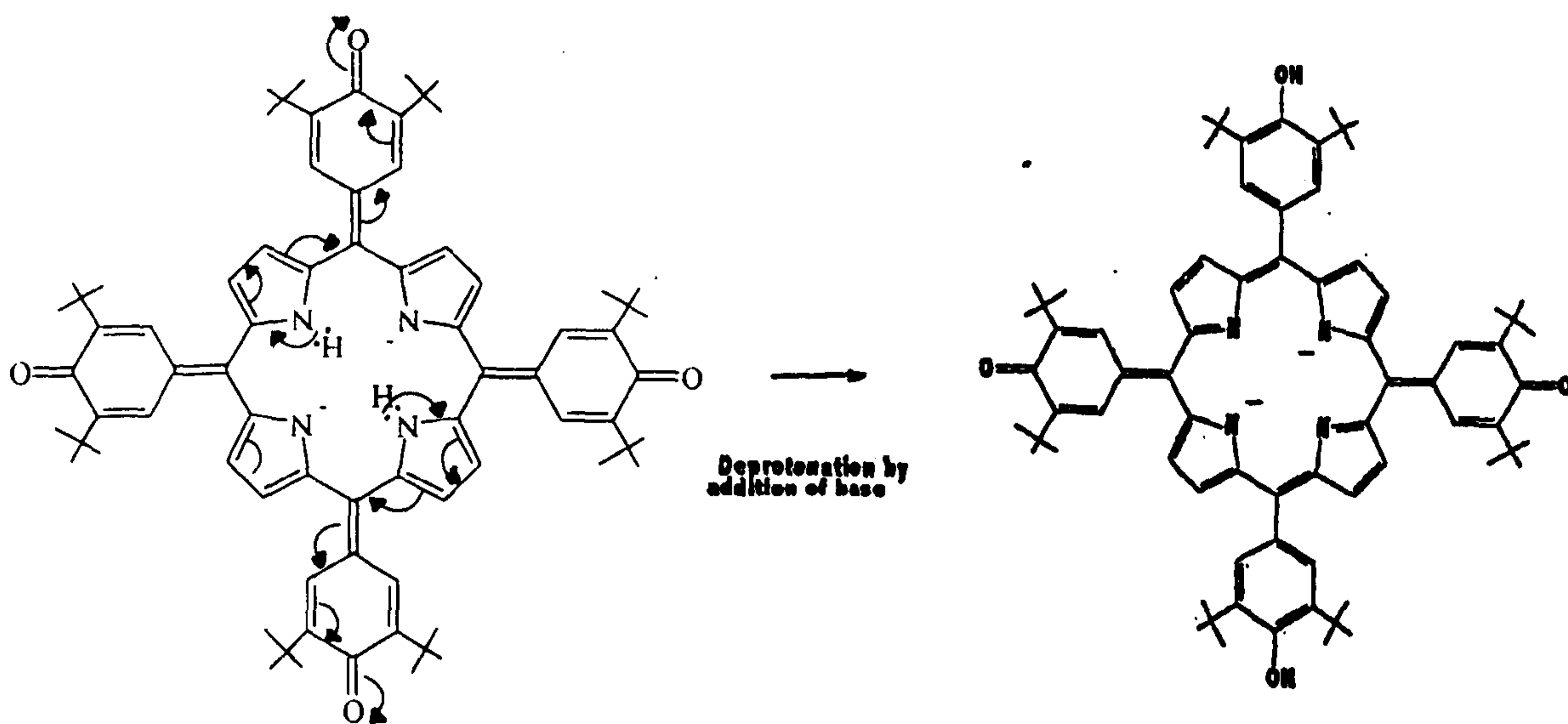
In solution, usually dichloromethane, the green amorphous powder gives a purple solution and this has been shown by n.m.r. studies to be the tautomeric, meso-bis 5,15-(3,5-di-t-butyl-4-hydroxyphenyl) - 10,20-(3,5,-di-t-butyl-4-oxacyclohexa-2,5-dienylene) porphodimethen **38a** (Scheme 4.3).



Scheme 4.3. Tautomerisation of Ox[T(DtBHP)P] as a result of dissolution.

The tautomer **38a** is the reactive species in the N-alkylation reaction and the addition of base results in a more reactive species as the phenoxide group produced delocalises its negative charge over two of the central nitrogens (Scheme 4.4).



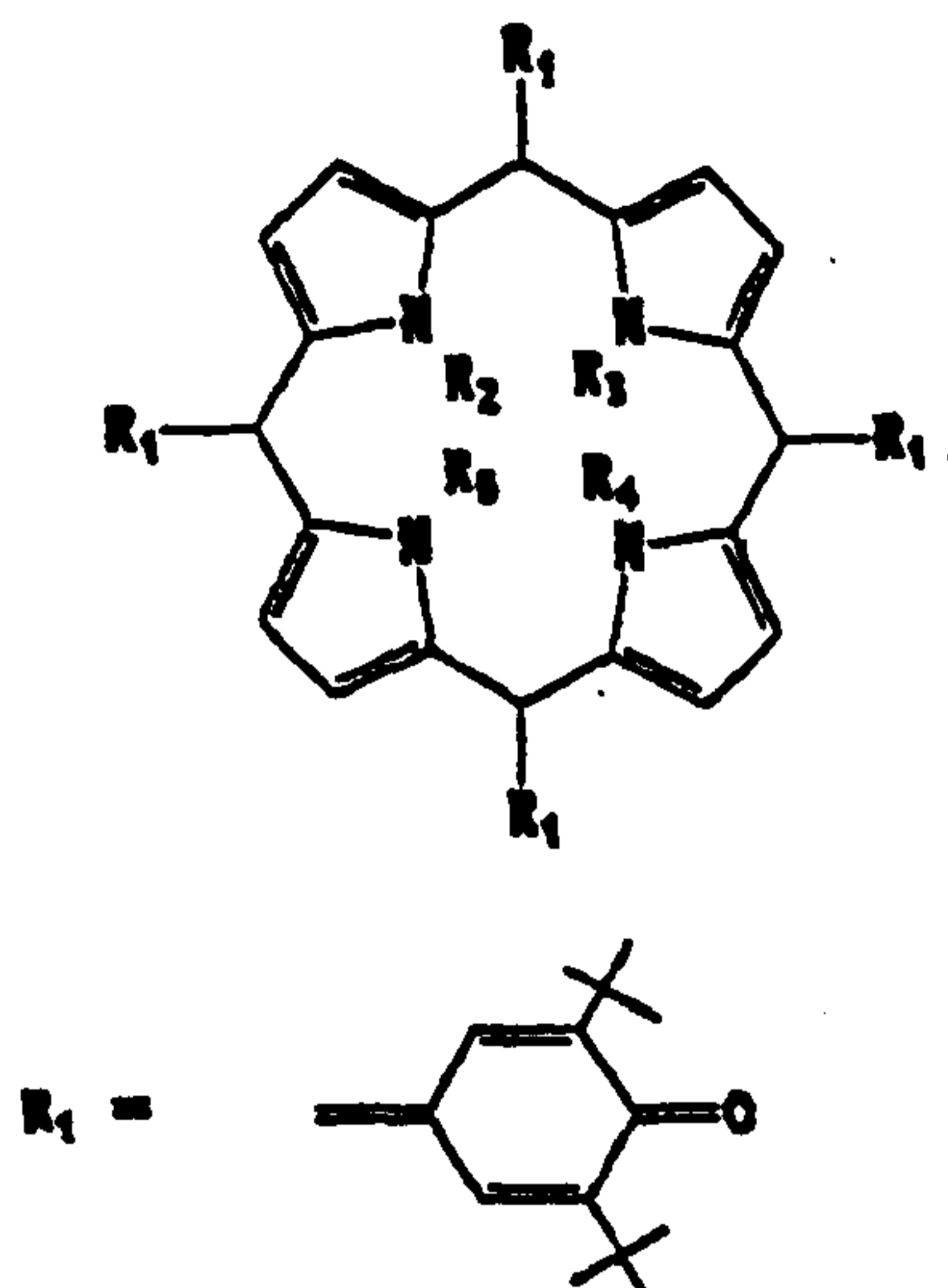


Scheme 4. 4. Delocalisation of phenoxide negative charge onto central nitrogen atoms.

The addition of a base to the oxidised porphyrin in solution does generate a more reactive species by the delocalisation of phenoxide negative charge and the deprotonation of the pyrrole type nitrogen atoms. In order to improve selectivity and maximize yields, attempts to N-alkylate the central nitrogens were carried out employing different solvents and by varying the strength of the base employed.



#### 4.4.2 N-alkylations of the oxidised porphyrin



	$R_2$	$R_3$	$R_4$	$R_5$
[38]	H	H	H	H
[39]	NBz	NBz	Nbz	NBz
[40]	NBz	H	NBz	H
[41]	Bx	Bx	Bx	Bx
[42]	ABz	ABz	ABz	ABz

NBz = Nitrobenzyl, Bx = Bromomethylbenzyl, ABz = Aminobenzyl.

#### 4.4.3 N-Alkylations in N,N'-Dimethylformamide

A series of alkylations were performed in N,N'-dimethylformamide employing different bases. The bases employed were methanolic KOH, potassium carbonate and caesium carbonate. The reactions were carried out in refluxing DMF as for the nitrobenzylation reaction<sup>(17)</sup> but each time differing the base. The percentage yields for the reactions for the di- and tetra derivatives are shown in Table 4.4.

Base Employed	di [40]	tetra [39]
Methanolic KOH	48%	3%
Potassium carbonate	-	-
Caesium carbonate	-	-

Table 4.4. % yields of N-nitrobenzylation reactions in DMF using different bases.

The results for the alkylation with methanolic KOH are consistent with those already reported<sup>(17)</sup>. The use of methanolic KOH produces a majority of the di-N-alkylate derivative [40] with low yields of the tetra derivative [39], enough only for identification purposes. Attempts to increase the selectivity and yields by changing the base to the metal carbonates proved to be unsuccessful. The use of the metal carbonates and DMF led to glue like mixtures, which on removal of solvents and subsequent chromatography, produced little or no products. DMF being a hygroscopic solvent reduces the efficiency of the base.

The reaction in DMF is employed if the di-N-alkylate derivative is desired. The reactions were carried out under identical conditions with different benzylic bromides. The same pattern was observed with the di-N-alkylated derivative being the predominantly formed species with methanolic KOH, and no reaction with the carbonates.

#### 4.4.4 N-Alkylations in Acetonitrile

A series of alkylations were carried out in dry acetonitrile, again employing different bases. A refluxing solution of the porphyrin in dry acetonitrile was treated with the different bases and benzylic bromides added. The results are shown in Table 4.5.

Base employed	Di [40]	Tetra [39]
Methanolic KOH	-	10%
Caesium carbonate	-	49%

Table 4.5. % yields of N-nitrobenzylation in acetonitrile using different bases.

The results indicate that by changing the solvent to acetonitrile and changing the base, the tetra derivative becomes more prevalent over the di-N-alkylate.

The change to the acetonitrile/caesium carbonate mixture leads to the selectivity of the tetra and in higher yields than previously reported. This discovery has led to the synthesis of some tetra-N-alkylates which were inaccessible before, or if formed, in extremely low amounts.

The UV/visible spectra of the N-alkylated oxidised porphyrins [39-42], show the characteristic signs of an oxidised porphyrin (Figure 4.9). Table 4.6 shows how the effect of substitution on the macrocycle nitrogens alters the absorption maxima. The identical shape and similar position of the oxidised porphyrins and the alkylated products in the UV/visible spectra suggest that alkylation occurs without altering the conformation of pyrrole rings in the xanthoporphyrinogen.

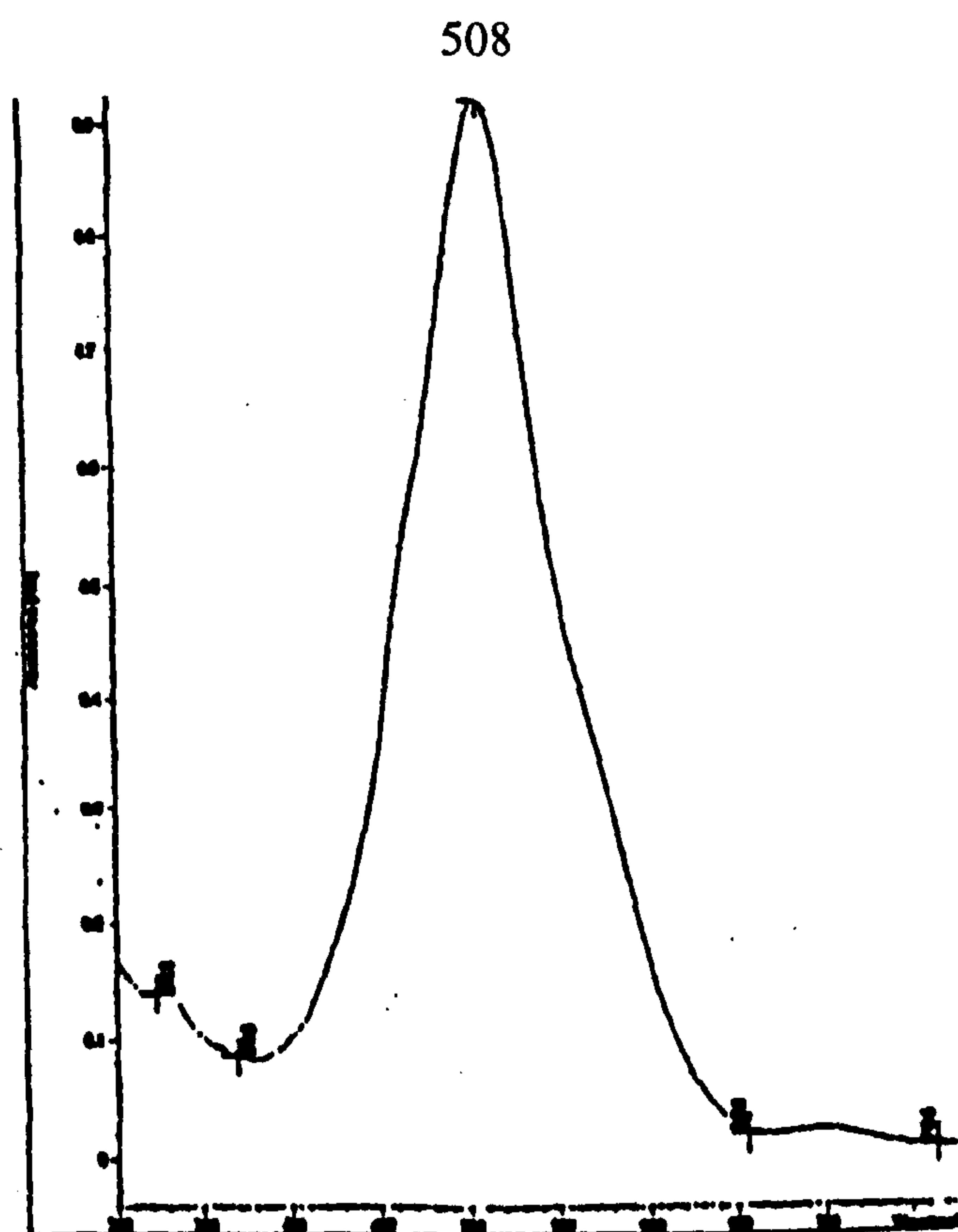


Figure 4.9. Electronic absorption spectra of Ox[T(DtBHP)P]

Oxidised Porphyrin	Absorption maximum
38	508
39	500
40	503
41	491
42	508

[38] - Meso-5,10,15,20-tetra-(3,5-di-t-butyl-4-oxacyclohexa-2,5-dienylene) porphyrinogen.

[39] - Meso-5,10,15,20-tetra-(3,5-di-t-butyl-4-oxacyclohexa-2,5-dienylene) N<sub>21</sub>,N<sub>22</sub>,N<sub>23</sub>,N<sub>24</sub>-tetra-4-nitrobenzylporphyrinogen.

[40] - Meso-5,10,15,20-tetra-(3,5-di-t-butyl-4-oxacyclohexa-2,5-dienylene) N<sub>21</sub>,N<sub>23</sub>-di-4-nitrobenzylporphyrinogen.

[41] - Meso-5,10,15,20-tetra-(3,5-di-t-butyl-4-oxacyclohexa-2,5-dienylene) N<sub>21</sub>,N<sub>22</sub>,N<sub>23</sub>,N<sub>24</sub>-tetra-4-bromomethylbenzylporphyrinogen.

[42] - Meso-5,10,15,20-tetra-(3,5-di-t-butyl-4-oxacyclohexa-2,5-dienylene) N<sub>21</sub>,N<sub>22</sub>,N<sub>23</sub>,N<sub>24</sub>-tetra-4-aminobenzylporphyrinogen.

Table 4.6. The effect of substitution on the electronic absorption maxima

The UV/visible spectra of the oxidised porphyrin [38] indicates the aromaticity of the porphyrin is interrupted by the oxidation. The B band and the four Q bands are replaced by a broad absorption which is considerably red shifted. The effect of the N-alkylations to the electronic absorption spectra are minimal. The spectra show the same broad absorption as for the oxidised porphyrin, but the absorption is shifted hypsochromically/bathochromically according to electron withdrawing/ donating power of the substituent. As expected, the substitution of an electron withdrawing group onto the central nitrogens produces a hypsochromic shift to the absorption band. As indicated in Table 4.7 the more electron withdrawing groups substituted on the central nitrogens the bigger the shift.

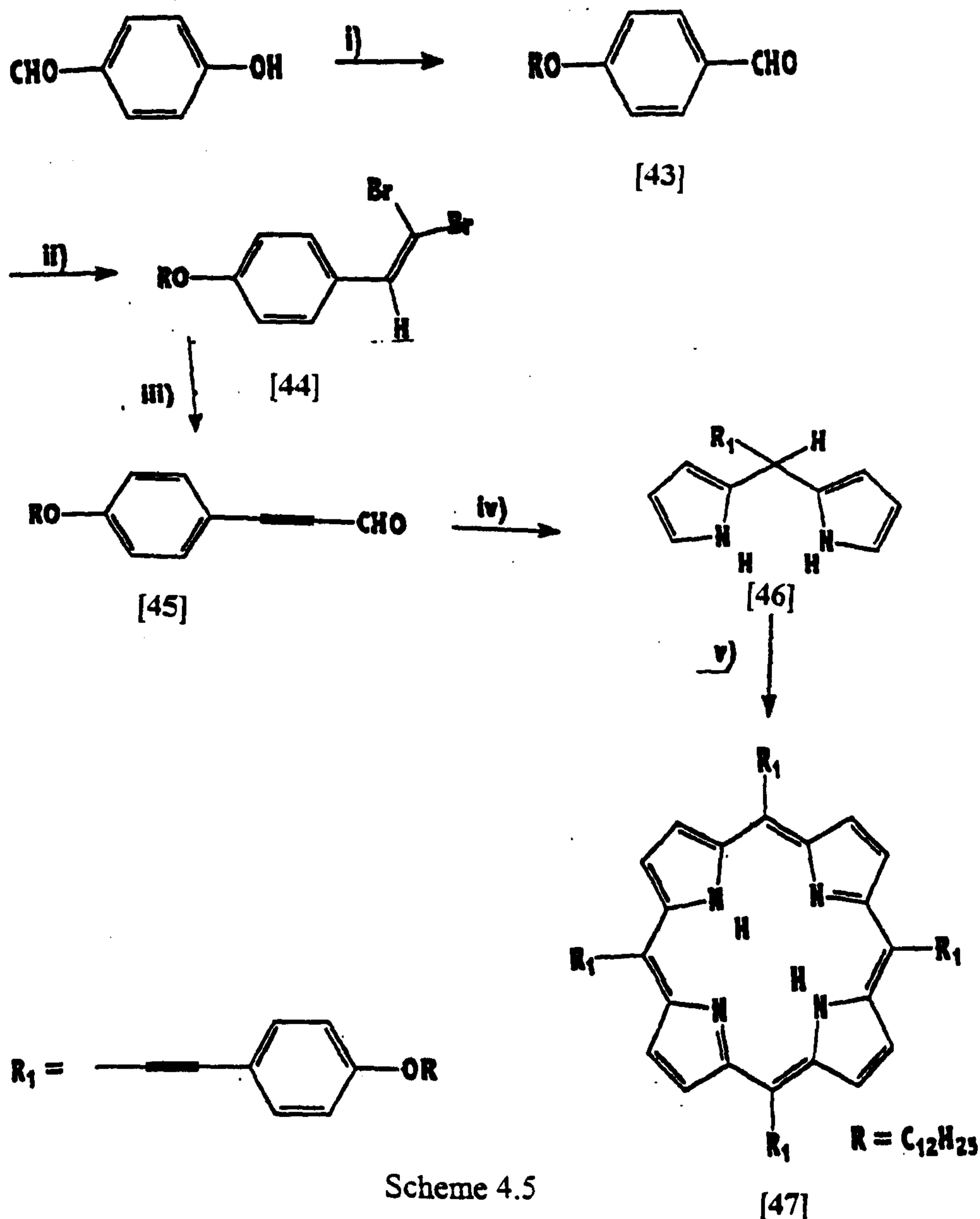
The nmr spectra of the oxidised porphyrin confirms the interruption of the aromaticity by the appearance of the N-H protons at a resonance at approximately 9.5 ppm. The porphyrin system with its conjugation produces a ring current which has a strong shielding effect on the protons. The N-H resonances are shifted upfield with respect to TMS, due to this shielding by the ring current, but on interruption of the macrocycles conjugated pathway the ring current is destroyed and so the shielding effect is diminished. This causes the N-H protons to shift down field which is shown in our oxidised and N-alkylated oxidised porphyrin spectra. The effect of substitution on the central nitrogens alters the nmr spectrum for the remaining proton resonances but only marginally. The effect of the electron withdrawing/donating group has the effect of shifting the proton resonances downfield/upfield.

#### 4.5 **Synthesis of Tetraethynylporphyrins**

The introduction of alkynyl groups into the porphyrin periphery has received a considerable degree of attention <sup>(19,20,21,22)</sup> in attempts to increase the conjugation effect between the porphyrin macrocycle and the aryl substituents. Initially, the porphyrin macrocycle was substituted with one or two alkynyl groups and the nonlinear optical activity studied. Meso-tetra-alkynyl porphyrins would be a useful addition to this group of compounds as the electronic interaction between the substituent and the porphyrin would be greater. When aryl groups are attached to the meso-position of a porphyrin they twist out of conjugation, but this is impossible with acetylenic groups. This should have an overall effect of increasing the electronic interaction between the porphyrin macrocycle and the peripheral substituents. Subsequently a series of meso-tetra (arylethynyl) porphyrins have been synthesised and their spectroscopic and nonlinear optical properties investigated.

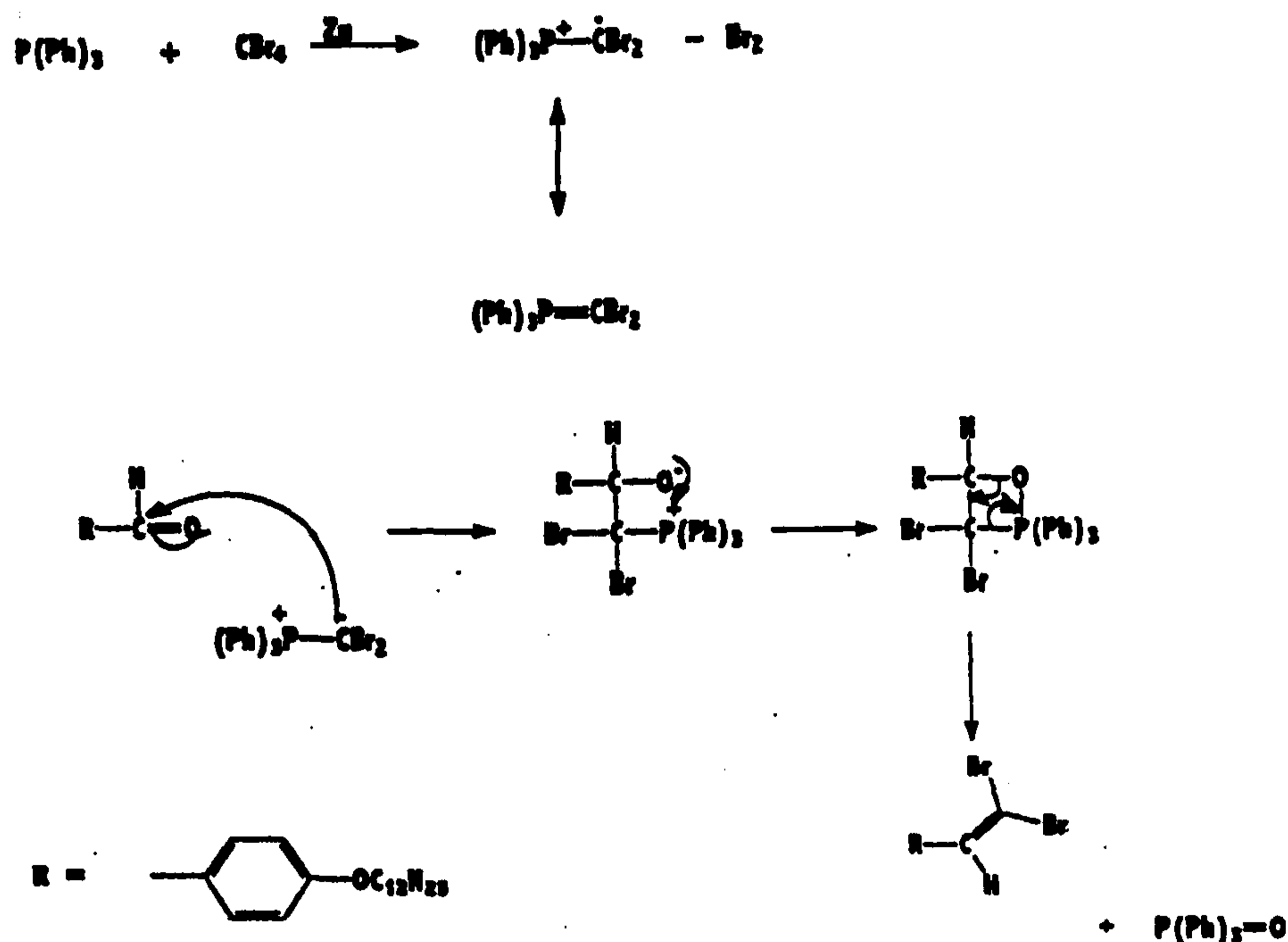
#### 4.5.1 5,10,15,20-meso-tetra (4-dodecyloxyphenylethynyl) porphyrin

The synthesis of the meso-tetra (arylethynyl) porphyrins was initially attempted via the Lindsey<sup>(23)</sup> porphyrin synthesis with pyrrole and the 4-dodecyloxyphenylpropynal [45], using  $\text{BF}_3 \cdot \text{OEt}_2$  as the catalyst. Upon oxidative work-up the desired porphyrin was observed by UV/visible absorption spectroscopy, but the desired product could not be isolated in high enough yields for suitable characterisation. The problems associated with low yields was solved in part using the two-pot procedure of Lee and Lindsey<sup>(24)</sup> (via a 5-substituted dipyrromethane). The meso-tetraarylethynylporphyrins were then synthesised using substituted arylpropynals (Scheme 4.5).



i)  $\text{C}_{12}\text{H}_{25}\text{Br}$ , DMF,  $\text{K}_2\text{CO}_3$ ,  $90^\circ\text{C}$ : ii)  $\text{Zn}/(\text{C}_6\text{H}_5)_3\text{P}/\text{CBr}_4/\text{DCM}$ : iii)  $\text{BuLi}$ , THF,  $-78^\circ\text{C}$ , DMF, RT,  $\text{H}^+/\text{H}_2\text{O}$ : iv) Xs pyrrole,  $\text{BF}_3 \cdot \text{OEt}_2$ , DCM: v)  $\text{BF}_3 \cdot \text{OEt}_2$ , I[45],  $-25^\circ\text{C}$ , DDQ.

The 4-dodecyloxyphenylpropynal **45** was prepared in a three step synthesis from 4-hydroxybenzaldehyde. Standard alkylation of the phenolic-OH with 1-dodecylbromide in DMF at 80-90°C yielded the 4-dodecyloxybenzaldehyde **43**. This was subsequently followed by a Corey and Fuchs reaction with CBr<sub>4</sub>, triphenylphosphine and zinc, (Scheme 4.6) to yield the appropriate β,β-dibromostyryl derivative **44**.



Scheme 4.6

The β,β-dibromostyryl derivative was extracted from the mixture with n-hexane and the by-product phosphine oxide, insoluble in n-hexane, is easily removed by filtration. Evaporation to dryness and column chromatography on silica gel results in the desired β,β-dibromostyryl derivative. The β,β-dibromostyryl derivative undergoes a low temperature reaction with two and a half equivalents of BuLi in THF, followed by quenching of the acetylide with DMF and acid hydrolysis, to yield the 4-dodecyloxyphenylpropynal **45**. Care was taken in controlling the pH of the reaction as the product was not formed if the pH dropped below pH 6-7 and during the acid hydrolysis step, care was taken not to allow the pH to rise above pH 6-7 as Michael addition reactions

occurred producing by-products. The arylpropynal was extracted from the mixture with diethylether, and separated easily by column chromatography on silica to give a yellow solid with yields in the range of 60-70%. As already mentioned, the Lindsey one-pot procedure was carried out with the arylpropynal 45 and pyrrole with  $\text{BF}_3 \cdot \text{OEt}_2$  as the catalyst, but yields were extremely low.

The Lee and Lindsey two-pot procedure was implemented whereby the arylpropynal was reacted with an excess of pyrrole and  $\text{BF}_3 \cdot \text{OEt}_2$  as the catalyst to produce the arylethynyl dipyrromethane. The arylethynyldipyrromethane was separated by column chromatography using a 1% solution of triethylamine in the eluent to ensure the dipyrromethane did not decompose on the column. The arylethynyldipyrromethane was prepared in high yield (>70%) and upon condensation with the corresponding arylpropynal at  $-25^\circ\text{C}$  in the presence of the  $\text{BF}_3 \cdot \text{OEt}_2$  catalyst and oxidative work-up with DDQ, the desired porphyrin 47 was synthesised.

The last step in the reaction is extremely sensitive to reaction conditions and therefore the exact concentration of catalyst, concentration of solvent, dryness of solvent and the reaction duration has to be implemented. A series of kinetic studies have been performed in order to maximise the reaction conditions. Also a series of reactions have been performed to maximise the yield in terms of concentration of solvent and catalyst.<sup>(25)</sup> The trend observed is one in which a concentration maximum is obtained, above which the yields start to decrease. Experiments<sup>(25)</sup> have been performed, where the catalyst concentration is increased/decreased and this showed that increasing the catalyst concentration at the start of the reaction had no effect on the yield but addition of catalyst after one hour of the reaction start time led to increased yields.

As reported earlier<sup>(26)</sup>, arylethynyl meso-substituents significantly red shift the porphyrin B and Q bands more than aryl substituents on their own.



Table 4.7 shows the comparison of the electronic absorption spectra of the meso-tetra (arylethynyl) porphyrin with some other porphyrin systems.

Porphyrin	$\lambda_{\max}/\text{nm}(\epsilon)^d$	Ref
H <sub>2</sub> TPP	419(470) 515(18.7) 548(8.1) 592(5.3) 647(3.4)	27
H <sub>2</sub> 1	451(371) 567(20.9) 606(5.5) 646(12.0)	26
H <sub>2</sub> 2	463 621 717	28
[47]	473(290) 655(90.2) 745(54.3)	

- H<sub>2</sub>TPP - Tetra-(phenyl)porphyrin  
H<sub>2</sub>1 - Tetra-(trimethylsilylethynyl) porphyrin  
H<sub>2</sub>2 - Tetra-(phenylethynyl) porphyrin  
[47] - Tetra (4-dodecyloxyphenylethynyl) porphyrin

Table 4.7

Table 4.7 shows that meso-alkynyl substituents significantly red-shift the porphyrin B and Q bands compared with that of tetraphenylporphyrin. Also replacing the trimethylsilyl group with an aryl group increases the red shift further and additional substitution to the attached phenyl group increase the red-shift further again. Also noticeable, is the increase in main Q band absorption relative to that of the B band. This illustrates a better communication between the porphyrin and aryl pi-systems when the ethynyl groups are introduced, than when the aryl group is connected directly to the porphyrin macrocycle.

The <sup>1</sup>H nmr spectrum of the meso-5,10,15,20-tetrakis-(4-dodecyloxyphenylethynyl) porphyrin strengthens the argument that the incorporation of meso-ethynyl groups increases the conjugation pathway due to

the downfield shift of the macrocycles proton resonances in the spectra. The singlet  $\beta$ -pyrrolic resonance has encountered a downfield shift of 0.27 ppm when compared to the  $\beta$ -pyrrolic resonances of 4-methoxytetraphenylporphyrin, a porphyrin system without the ethynyl groups. As already mentioned, an increase in conjugation will cause a downfield shift and this therefore confirms that the addition of ethynyl groups increases the communication between porphyrin and aryl pi-systems.

#### **4.5.2 Metallations of the 5,10,15,20-tetra-(4-dodecyloxyphenylethynyl) porphyrin**

A series of metallations were performed on the porphyrin macrocycle using the literature methods for metal insertions <sup>(9)</sup>. The metals inserted covered a wide range of transition metals including Mn, Ni, Pd, Cu and Zn. The zinc copper and palladium porphyrins were synthesised by treating a solution of the porphyrin in chloroform at 50-60°C with a saturated solution of the metal acetate in methanol and the reaction followed by UV/visible spectroscopy. The nickel and manganese porphyrins were synthesised by treating a refluxing solution of the porphyrin in DMF with the appropriate metal II chloride and monitoring the reaction by UV/visible spectroscopy. The porphyrins were subjected to column chromatography to isolate a pure metallated porphyrin, free from any unreacted free base porphyrin. The metallated porphyrins, like that of the parent free base porphyrin, were isolated as green solids with yields ranging from 33%→85% and they showed the characteristic UV/visible spectra for metallated porphyrins (Table 4.8).

Porphyrin	$\lambda_{\text{max}}/\text{nm}(\epsilon \cdot 10^3)$			% Yield
<b>47</b>	473 (290)	655(90)	745 (54)	-
<b>48</b>	483(253)	635(15)	689(43)	85
<b>49</b>	478(239)	620(11)	666(36)	83
<b>50</b>	476(236)	597(15)	648(39)	65
<b>51</b>	475(267)	593(18)	644(53)	33
<b>52</b>	458 (109)	513(189)	730(66)	56

[47] - 5,10,15,20-tetra-(4-dodecyloxyphenylethynyl)porphyrin

[48] - 5,10,15,20-tetra-(4-dodecyloxyphenylethynyl)porphyrinatozinc

[49] - 5,10,15,20-tetra-(4-dodecyloxyphenylethynyl)porphyrinatocopper

[50] - 5,10,15,20-tetra-(4-dodecyloxyphenylethynyl)porphyrinatonicel

[51] 5,10,15,20-tetra-(4-dodecyloxyphenylethynyl)porphyrinatopalladium

[52] - 5,10,15,20-tetra-(4-dodecyloxyphenylethynyl)porphyrinatomanganese

Table 4.8

As Table 4.8 shows, the insertion of different metal ions into the porphyrin macrocycle has pronounced effects on the relative shifts and intensities of the porphyrins B and Q bands. The metals cover a wide range of the transition metal series and include metals which can be classed in the groups regular, irregular, hypso and hyper. The metals inserted show shifts and intensity changes that are consistent with literature results reported for metal insertions into porphyrin systems that have no ethynyl groups attached. The zinc porphyrin classed as a regular porphyrin with its  $d^{10}$  electronic configuration follows the usual trend with a red shift of the B band some 10nm.

There are slight wavelength shifts among the remaining metalloporphyrin spectra and  $\lambda$  increases along the series Pd<Ni<Cu<Zn and this is consistent with literature findings.<sup>(27)</sup> The manganese porphyrin falls into the hyper group with its  $d^4$  electronic configuration and the UV/visible spectra of the Mn(III)

porphyrin is consistent with literature findings resulting in large shifts and additional weak bands observed.

#### 4.5.3 Reactions at the porphyrin periphery

##### (a) Bromination of [47]

The bromination reaction was carried out according to the standard literature method for porphyrin bromination <sup>(28)</sup>. The only difference in the reaction conditions is that of temperature. In the literature procedure the reaction is carried out at reflux conditions, whereas in our experiment the bromination is carried out at 0°C. It is postulated that as a result of the increased delocalisation throughout the system, the  $\beta$ -pyrrolic positions will become more susceptible to electrophilic attack.

To a solution of the porphyrin in carbon tetrachloride at 0°C (ice bath), a solution of N-bromosuccinimide in THF was added with a slight excess (1ml) of pyridine. Throughout the duration of the experiment the reaction was shielded from direct light and the reaction was stopped after twenty minutes. The reaction produced a complex mixture of porphyrins which required careful column chromatography to isolate the desired porphyrin.

The 2-bromo-5,10,15,20-meso-tetra-(4-dodecyloxyphenylethynyl) porphyrin [53] is isolated as a green solid with a yield of approximately 50%. The addition of the bromine group to the porphyrin has a considerable effect on the UV/visible spectrum as shown in Table 4.9.

Porphyrin	$\lambda_{nm}$		
[47]	473 (290)	655(90.2)	745(54.3)
[53]	468 (459)	633(99)	724(49)

Table 4.9

As expected, the electron withdrawing effect of the bromo group has an hypsochromic effect on the electronic absorption spectrum and the B and Q bands are blue shifted.

The introduction of the bromine group to the porphyrin macrocycle has a considerable effect on the  $^1\text{H}$  nmr spectrum by producing an unsymmetrical compound (Figure 4.10).

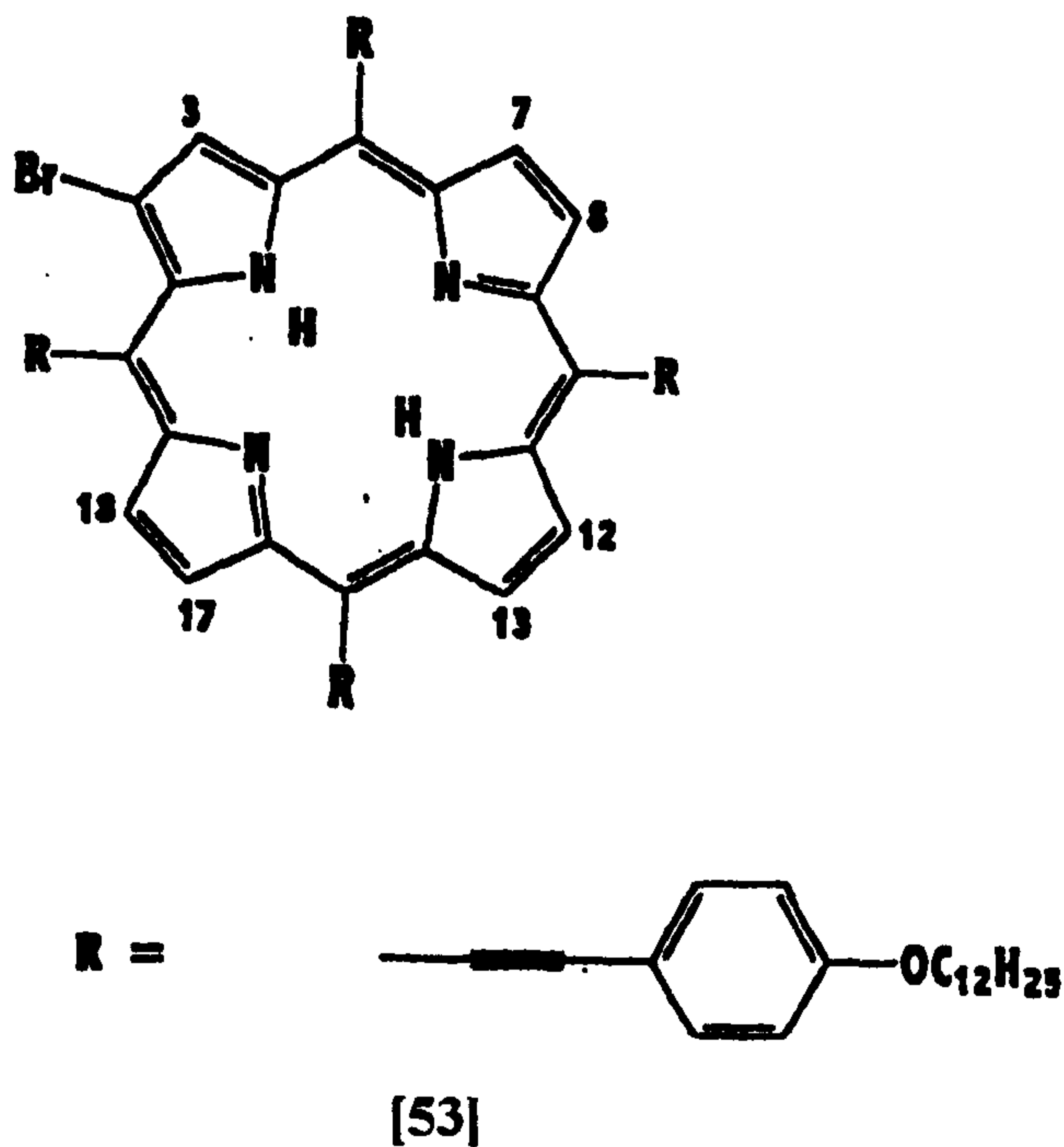


Figure 4.10

Due to the unsymmetrical nature of the porphyrin, the simple  $^1\text{H}$  nmr experienced for the symmetrical porphyrin is replaced by a complex mixture of singlets and doublets associated with unsymmetrical porphyrins.

The singlet shown by the  $\beta$ -pyrrolic-H in the symmetrical porphyrin is replaced by a series of singlets and doublets. The first noticeable feature of the  $\beta$ -pyrrolic resonances is that they have shifted downfield on the introduction of an electron-withdrawing group, which is to be expected. The electron-withdrawing group has a deshielding effect and hence downfield shifts. In going from the symmetrical to the unsymmetrical porphyrin, by introducing the bromine group the shift for the  $\beta$ -pyrrole resonance is from 9.13 ppm  $\rightarrow$  9.45 ppm. The splitting pattern gives a doublet, singlet, doublet, doublet which are of the intensities 2:1:2:2 which account for the protons  $\text{H}_{7,8}$ ,  $\text{H}_3$ ,  $\text{H}_{17,18}$  and  $\text{H}_{12,13}$  respectively. The unsymmetrical nature of the porphyrin also affects the splitting pattern of the phenyl rings attached to the ethynyl group. Instead of one AB spin system as experienced for the symmetrical porphyrin, the phenyl rings are now in different environments. The two phenyl rings adjacent to the pyrrole ring with the bromine attached are shifted downfield due to the closeness of the bromine group and so two separate AB spin systems are visible for the phenyl rings attached at  $\text{C}_{20}$  and  $\text{C}_5$  position. The phenyl rings attached to the meso-positions  $\text{C}_{10}$  and  $\text{C}_{15}$  are not really affected by the bromine group and appear as the same AB spin system, they appear to be in the same environment, and these are at the same resonance as those encountered for the symmetrical porphyrin. The long chain alkyl groups are not significantly affected by the bromine group, but the N-H protons are. Again, the deshielding affect of the bromine group causes the proton resonances to shift downfield from -2.89ppm  $\rightarrow$  -1.65ppm.

The noticeable points to be taken from this reaction are:

- i) the reaction temperatures and
- ii) the reaction time.

The reaction proceeds to completion reasonably quickly and at temperatures considerably lower than the reflux temperatures used for porphyrin systems lacking ethynyl substituents. This does suggest that the porphyrin macrocycle is more activated towards electrophilic attack as a result of the increased delocalisation caused by the introduction of the ethynyl group.

The bromination of the meso-(arylethynyl) porphyrin was reproducible on repeated experiments, under identical conditions, with the bromine substituting at the two position of the macrocycle.

#### **(b) Nitration**

The nitration of the 5,10,15,20-tetra-meso-(4-dodecyloxyphenylethynyl) porphyrin was attempted using several nitrating agents and under various nitrating conditions.<sup>(29)</sup> Attempts to isolate any compound for characterisation and identification proved unsuccessful. Upon addition of the particular nitrating agent to a solution of the porphyrin in dichloromethane, the beautiful green colour associated with the tetra-(arylethynyl) porphyrin was immediately lost. This would suggest that the nitrating agent was attacking the ethynyl position and not the desired  $\beta$ -pyrrolic position. Attempts to extract any characterisable product from this reaction proved unsuccessful. UV/visible spectroscopy of the reaction mixture proved inconclusive as the characteristic spectra of the green tetra-(arylethynyl) porphyrin collapsed as the reaction mixture became a brown colour.

#### **c) Formylation**

The introduction of the formyl group into the porphyrin's periphery was attempted using the Vilsmeier formylation reaction.<sup>(30)</sup> The reaction was attempted on the free-base porphyrin and the copper derivative. The porphyrin was treated with the Vilsmeier complex formed from dimethylformamide

(DMF) and phosphorus oxychloride (POCl<sub>3</sub>) in dichloromethane and refluxed. The mixture was poured into water and made alkaline to pH 9-10, then the organic layer separated. UV/visible spectroscopy at this stage showed, as for the nitration reaction, that the characteristic tetra-(arylethynyl) porphyrin spectrum had disappeared, as once again the characteristic green colour, associated with the ethynyl porphyrins in solution, was replaced by a light brown colour. Once again, this suggests that the reaction is not occurring at the desired  $\beta$ -pyrrolic position but at the triple bond position. The reaction was also carried out with the copper derivative, but like that of the free-base porphyrin, the reaction did not occur at the desired  $\beta$ -pyrrolic position. All attempts to isolate any characterisable product proved unsuccessful.

#### 4.5.4 Improved synthesis of (arylethynyl) porphyrins using protection chemistry

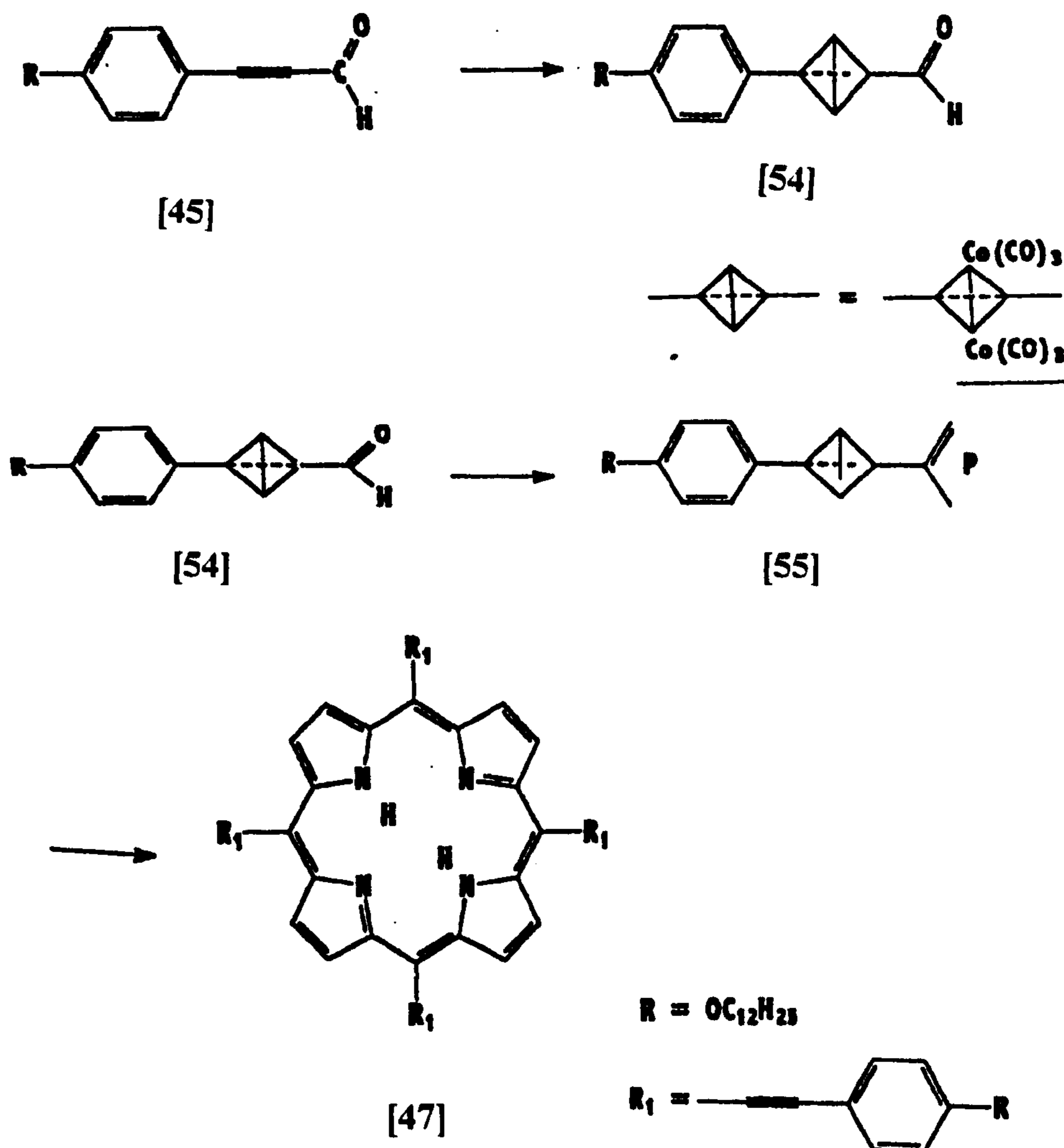
In the one-pot synthesis of the tetra-(arylethynyl) porphyrins, the presence of the ethynyl groups appear to decrease porphyrin yields. Also, the range of porphyrins synthesised, is limited to those <sup>(31)</sup> capable of solubilisation in chlorinated solvents. Attempts have been made to synthesise water soluble porphyrins, where the alkyl chains are reduced to methoxy - and hydroxy -, but these have proved unsuccessful because the precursors precipitate from the dichloromethane reaction mixture prior to cyclisation.

In an attempt to improve porphyrin yields and access the less soluble porphyrin systems, it was decided to protect the ethynyl groups at the aldehyde stage with the use of dicobalt octacarbonyl.

##### i) **meso-5,10,15,20-tetra-(4-dodecyloxyphenylethynyl) porphyrin**

The porphyrin was synthesised by protecting the acetylene group at the aldehyde stage, and a one-pot synthesis performed (Scheme 4.7).





Scheme 4.7

The arylpropynal was stirred in THF with  $\text{Co}_2(\text{CO})_8$  at room temperature until effervescence (of CO) ceased. The product was purified by column chromatography to yield the  $\text{Co}_2(\text{CO})_6$  - ethynyl-protected aldehyde **54** which, like  $\text{Co}_2(\text{CO})_8$ , was chocolate brown in colour. The product was characterised by  $^1\text{H}$  nmr and IR. This showed the loss of the characteristic ethynyl stretch at  $2196\text{ cm}^{-1}$ , and the appearance of terminal carbonyl groups centred around  $2062\text{ cm}^{-1}$ . The proton nmr showed a downfield shift of 1ppm for the aldehyde proton, now deshielded due to the loss of the ethynyl moiety.

The protected aldehyde **54** was reacted with an equimolar amount of pyrrole using  $\text{BF}_3 \cdot \text{OEt}_2$  as a catalyst according to the Lindsey conditions.<sup>(24)</sup> After oxidative workup with DDQ, a chocolate brown solution remained, and this was subjected to column chromatography on silica gel to yield the meso-

5,10,15,20-tetra-(Co<sub>2</sub>(CO)<sub>6</sub>-ethynyl-protected) porphyrin **55**. When the brown tlc spot was exposed to light it eventually turned green, indicating the presence of the deprotected porphyrin, therefore, the column chromatography was performed without exposure to light, to prevent deprotection on the column and hence mixtures. UV/visible spectroscopy gave no clear indication of porphyrin, as the usual sharp B and Q bands were indistinct, with exceptionally broad, weak bands observed around 420 and 500-650nm instead. To confirm the Co<sub>2</sub>(CO)<sub>6</sub>-protected porphyrin had been synthesised, a parallel reaction was performed where the previously prepared arylethynyl porphyrin was treated with Co<sub>2</sub>(CO)<sub>8</sub>. The green colour associated with the arylethynyl porphyrin was replaced by a chocolate brown solution which gave extremely broad, weak UV/visible bands in the 420nm and 500-650nm regions. The <sup>1</sup>H nmr spectrum and microanalysis finally confirmed we had the Co<sub>2</sub>(CO)<sub>6</sub>-ethynyl-protected porphyrin.

The deprotection was performed by using iron(III) perchlorate to oxidatively deprotect the Co<sub>2</sub>(CO)<sub>6</sub>-protected ethynyl. Literature methods<sup>(32)</sup> used ceric ammonium nitrate (CAN), but this destroyed the porphyrin macrocycle. Thus an excess of the iron(III) perchlorate in methanol was added to the brown solution of the porphyrin in DCM, producing a deep green solution, which was subsequently subjected to column chromatography. This gave a good yield of the tetra-(4-dodecyloxyphenylethynyl) porphyrin (43% from aldehyde **45**); a 14 fold increase in yield over the previous one-pot route.

ii). **meso-5,10,15,20-tetra-(4-methoxyphenylethynyl) porphyrin**

As already mentioned, the synthesis of the less soluble (4-methoxyphenyl ethynyl) porphyrin has proved impossible because of the insolubility of porphyrin precursor prior to cyclisation.

The 4-methoxyphenylpropynal **57** is prepared in an analogous fashion to the dodecyloxy-derivative by the Corey and Fuchs reaction of 4-

methoxybenzaldehyde to form the  $\beta,\beta$ -dibromostyryl derivative **56**. This undergoes the low temperature reaction with BuLi, followed by quenching of the acetylide with DMF and acid hydrolysis to yield the 4-methoxyphenylpropynal in 60% yield. The arylethynyl aldehyde was then taken to synthesise the 4-methoxyphenylethynyl dipyrromethane in 76% yield, and the one-pot and two-pot procedures were implemented. Both procedures resulted in no porphyrin formation. The characteristic green colour of the porphyrin in dichloromethane, upon oxidation work-up with DDQ was not observed as a result of the porphyrinogen being insoluble in the chlorinated solvent.

Protecting the ethynyl groups with  $\text{Co}_2(\text{CO})_8$  prior to the porphyrin synthesis increases the solubility of the porphyrin. This allows the synthesis of the inaccessible 4-methoxy derivative to be achieved. The 4-methoxyphenylpropynal is protected with  $\text{Co}_2(\text{CO})_8$ , as for the dodecyl derivative, in THF at room temperature to give yields around 85%.

Characterisation was achieved once again by  $^1\text{H}$  nmr and IR and this gave almost identical results as the dodecyl- derivative.

The porphyrin was synthesised with an equimolar amount of pyrrole under Lindsey conditions using  $\text{BF}_3\cdot\text{OEt}_2$  as the catalyst. Oxidative work-up with DDQ resulted in a red/brown solution, which was subsequently subjected to column chromatography to yield the desired meso-5,10,15,20-tetra-(4-methoxyphenyl- $\text{Co}_2(\text{CO})_6$ -ethynyl-protected) porphyrin **61** in 45% yield.

UV/Visible spectroscopy, like that for the dodecyl-derivative, proved inconclusive with its broad, weak bands.  $^1\text{H}$  nmr spectroscopy, IR and microanalysis confirmed the desired product had been attained.

The deprotection, following the TLC observation, was performed by adding a few drops of tetrabutylammonium hydroxide to the porphyrin dissolved in DCM, and exposed to light and oxygen for several hours. As the porphyrin slowly deprotected the characteristic red/brown colour of the protected

porphyrin began to disappear, and a solid precipitated from the solution. The precipitate was filtered to yield a green/black solid in 81% yield, but attempts to characterise the solid proved unsuccessful as the solid was insoluble in practically all solvents. The problem with the unprotected synthesis was one of solubility of the porphyrinogen. The protected ethynyl procedure enables the formation of the porphyrin but this also has solubility problems.

iii). **meso-5,10,15,20-tetra-(4-hydroxyphenylethynyl) porphyrin**

The synthesis of the 4-hydroxy-derivative was attempted by the demethylation of the  $\text{Co}_2(\text{CO})_6$ -ethynyl-protected porphyrin 61 using boron tribromide.

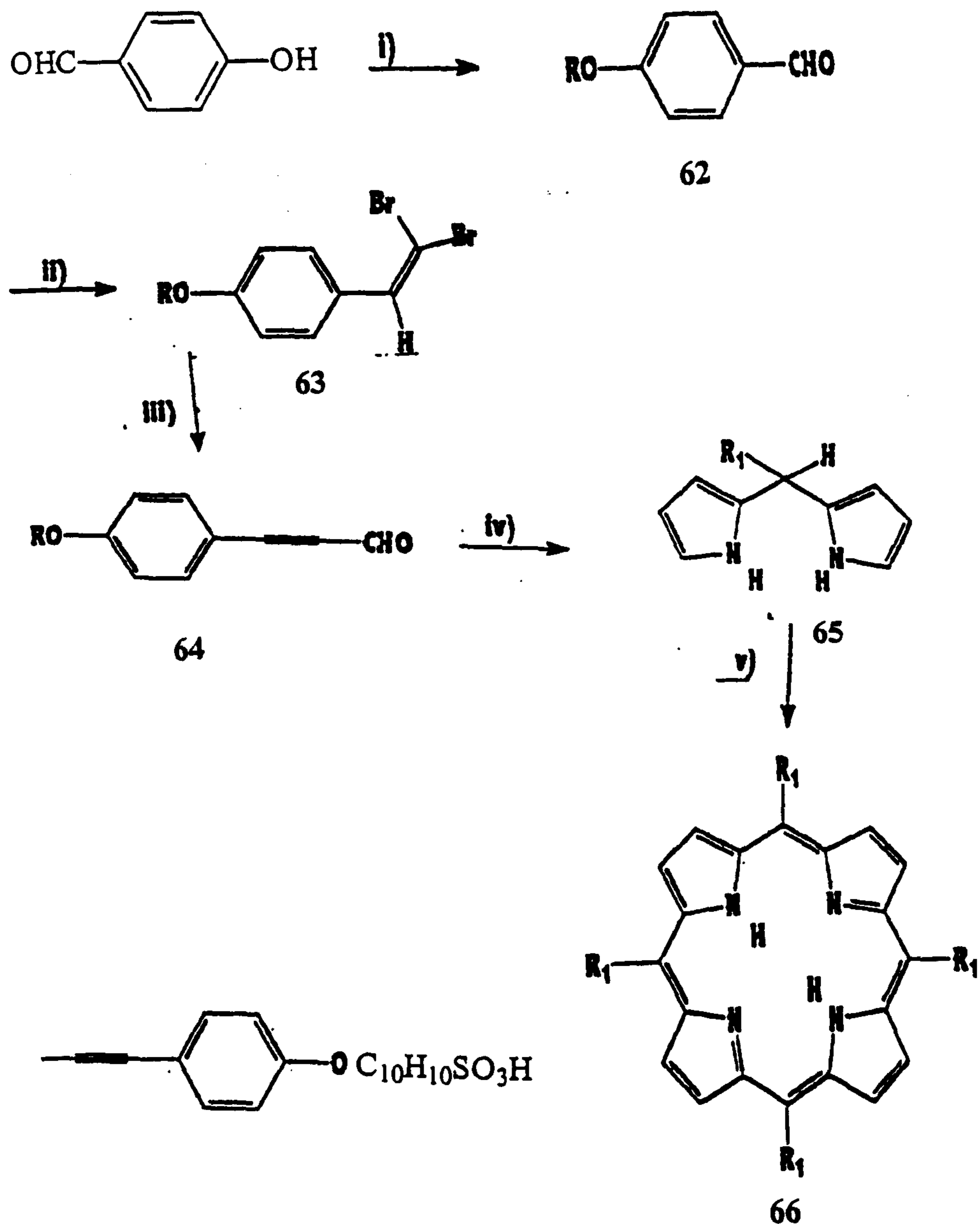
A solution of the protected-ethynyl porphyrin in DCM was treated with boron tribromide at  $-80^\circ\text{C}$ . On work-up the isolation of a green/black solid was obtained as it precipitated out of solution. The reaction with  $\text{BBr}_3$  appears to demethylate and deprotect in one step with the isolation of the tetra-4-hydroxyphenylethynyl porphyrin as a green/black solid. Like the 4-methoxy derivative, the 4-hydroxy is also insoluble in practically all solvents. The only clear indication the 4-hydroxy porphyrin had been synthesised, was to take the porphyrin and reflux it in DMF with 1-dodecyl bromide and potassium carbonate. The alkylation of the 4-hydroxy groups generated the previously synthesised tetra-(4-dodecyloxyphenylethynyl) porphyrin which was characterised by UV/visible spectroscopy.

The added solubility afforded by the  $\text{Co}_2(\text{CO})_6$ - protecting groups in the cyclisation step, permitted the production of the less soluble porphyrins not prepared by the previous routes. Unfortunately, the synthesised porphyrins will have limited uses, due to the solubility problems incurred upon them by the shorter chain length.

#### 4.5.4 Synthesis of potentially water-soluble tetra-(arylethynyl) porphyrins

Attempts to synthesise water-soluble (arylethynyl) porphyrins by reducing the chain length of the substituted alkoxy groups to 4-methoxy and 4-hydroxy proved unsuccessful. It was decided to try a completely different approach by the addition of water solubilising groups, the sulphonates.

##### meso-5,10,15,20-tetra-(4-decyloxyphenylethynyl)porphyrinsulphonate



i)  $\text{C}_{10}\text{H}_{19}\text{O}$ , DMF,  $\text{K}_2\text{CO}_3$ ,  $90^\circ\text{C}$ : ii)  $\text{Zn}/(\text{C}_6\text{H}_5)_3\text{P}/\text{CBr}_4/\text{DCM}$ : iii) BuLi, THF,  $-78^\circ\text{C}$ , DMF, RT,  $\text{H}^+/\text{H}_2\text{O}$ : iv) Xs pyrrole,  $\text{BF}_3 \cdot \text{OEt}_2$ , DCM: v)  $\text{BF}_3 \cdot \text{OEt}_2$ , 64,  $-25^\circ\text{C}$ , DDQ.

The synthesis of a water soluble porphyrin with sulphonate groups was achieved in a seven step procedure starting from 4-hydroxybenzaldehyde. The initial steps were carried out in the same way as for the previous arylethynyl-derivatives except that the initial alkylation of 4-hydroxybenzaldehyde was reacted with 1,10-diiiododecane. The product of this reaction was the 4-(1-iododecyloxy) benzaldehyde **62** and this was isolated as a white solid, (75% yield), after column chromatography. The target aim was to synthesise the 4-(1-iododecyloxy) phenylpropynal **64** and this was achieved by the same route used for the previously synthesised arylpropynal derivatives. The 4-(1-iododecyloxy)-benzaldehyde **62** undergoes the Corey and Fuchs reaction to yield the appropriate  $\beta,\beta$ -dibromostyryl derivative **63** in 80% yield. This isolated white solid is then subjected to the low temperature reaction with BuLi, subsequent quenching with DMF and acid hydrolysis to yield the 4-(1-iododecyloxy) phenyl propynal **64** as a yellow solid, yield approximately 65%.

The two-pot procedure of Lee and Lindsey was the preferred route to the tetra-(arylethynyl) porphyrin. Therefore, the 4-(1-iododecyloxy) phenyl ethynyl dipyrromethane **65** was synthesised by reacting the previously synthesised arylethynylpropynal **64** with an excess of pyrrole in the presence of a  $\text{BF}_3 \cdot \text{OEt}_2$  catalyst. The dipyrromethane was isolated as a brown solid in yields greater than 80%. The arylethynyl dipyrromethane **65** was reacted with an equimolar amount of the arylethynylpropynal **64** in DCM at  $-25^\circ\text{C}$  using  $\text{BF}_3 \cdot \text{OEt}_2$  as the catalyst. Upon oxidative work-up with DDQ the characteristic green colour associated with the arylethynyl porphyrins in solution was observed and this was confirmed by UV/visible spectroscopy. The mixture was concentrated and subjected to column chromatography on silica gel to yield the desired meso-5,10,15,20-tetra-(4-(1-iododecyloxyphenyl)ethynyl) porphyrin **66** as a green solid (yield 12%). The UV/visible electronic spectrum of the porphyrin gave the characteristic red shift associated with tetra-(arylethynyl) porphyrins. In comparison to the other symmetrical porphyrin **47** synthesised previously, the UV/visible spectra are almost identical. The  $^1\text{H}$  nmr of both the symmetrical porphyrins are almost identical, with slight downfield shifts for the

iodo- porphyrin. This is to be expected as the iodo-group with its electron withdrawing effect will have a deshielding effect and hence downfield shifts. The downfield shifts are only minor and this indicates that the iodo groups are only having a minor effect on the porphyrin, due mainly to its isolated location at the end of the alkyl chain. The composition of the porphyrin was confirmed by FABS-MS and microanalysis.

In order to attach the sulphonate groups, zinc metal was inserted into the centre of the porphyrin macrocycle. This was achieved using the standard procedures for metallations<sup>(9)</sup>. To a solution of the porphyrin in chloroform, at 50°C, a saturated solution of zinc acetate in methanol was added and the reaction monitored by UV/visible spectroscopy.

The uv/visible and <sup>1</sup>H nmr spectra of the zinc porphyrin [67] were characteristic of zinc porphyrins. The porphyrin was characterised by FABS-MS and microanalysis.

The water solubilising groups were added on to the porphyrin by the literature method<sup>(33)</sup> for the addition of sulphonate groups. The zinc porphyrin was dissolved in 1ml of freshly prepared dioxane and brought to reflux. Tetraethylammoniumsulphite (1ml) was added and the mixture refluxed. After removal of solvent, a green solid was isolated, which was subsequently triturated with acetone, then filtered. The solid residue was then washed with sodium chloride, sodium perchlorate to yield a green solid. UV/visible spectroscopy was performed on the water soluble tetra-(arylethynyl) porphyrin [68] with a broad solet band centred around 470 nm. The yield was only sufficient for initial characterisation by uv/visible spectroscopy.

#### **4.5.5 Synthesis of arylethynyl porphyrins containing electron withdrawing and electron donor groups**

(1) The porphyrins synthesised with the arylethynyl groups attached have all been prepared utilising the arylethynyl dipyrromethanes and aryl propynals

with the same substitution pattern. This eventually results in symmetrical porphyrins with the same substituent groups attached to the meso positions, and the only way to introduce an unsymmetrical environment is to perform reactions on the porphyrin periphery i.e. bromination, nitration etc. As already observed, these reactions have not proved to be too successful and in an attempt to synthesise arylethynyl porphyrins that have a degree of unsymmetricality with different substituent groups on the porphyrin periphery, the Lee and Lindsey procedure<sup>(24)</sup> was implemented whereby an arylethynyl dipyrromethane is reacted with a variety of propynals. This results in trans-disubstituted meso-tetraethynyl porphyrins, with one type of ethynyl moiety in the 5,15- positions and another in the 10,20-positions. This does not introduce an element of unsymmetricality to the porphyrin system, but it is a convenient route to introducing electron donor/acceptor groups to the porphyrin periphery.

**(2) Meso 5,15-bis (4-dodecyloxyphenyl ethynyl) - 10,20-bis (4-nitro phenylethynyl) porphyrin**

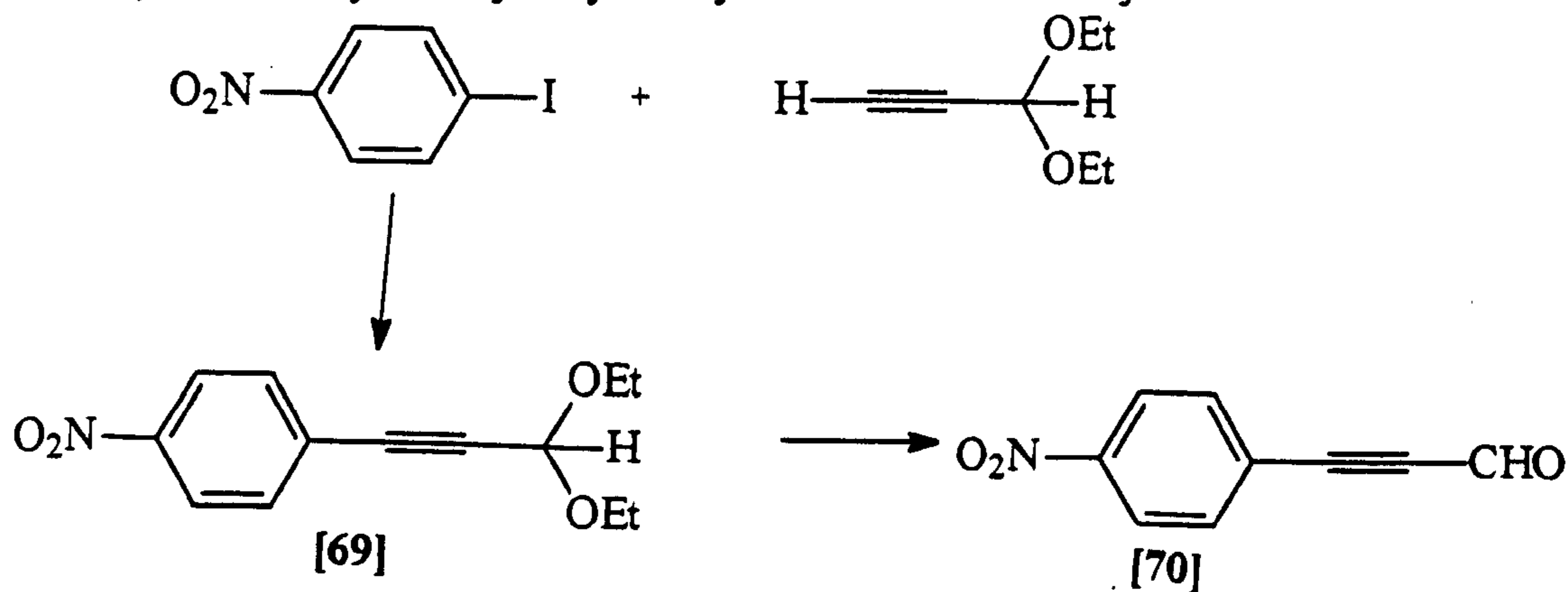
The title compound was chosen since the synthesis of the electron donating 4-dodecyloxyphenylethynyl moiety had been previously well documented and the 4-nitro electron withdrawing groups have received considerable attention due to the wealth of research interests that have been performed previously. The synthesis of the 4-dodecyloxyphenylpropynal **45** has been reproduced several times and the synthetic route has been reported earlier in this chapter. The ease of formation and high yields encountered, coupled with the fact that the arylethynyl dipyrromethane **46** is easily accessible was a key determinant in choosing this derivative as the electron donating group. The 4-nitrophenyl-electron withdrawing group has been used extensively in donor/acceptor systems as the nitro is a good withdrawing group. The use of 4-nitrophenylethynyl- groups as electron-withdrawing substituents is not so well documented and so the formation of the 4-nitrophenylpropynal was looked at.



## 4-Nitrophenylpropynal

The synthesis of 4-nitrophenylpropynal was attempted following the procedure described for the aryl propynal derivatives (Scheme 4.6) already prepared in this chapter. Subsequently, 4-nitrobenzaldehyde was subjected to the Corey and Fuchs reaction to form the  $\beta,\beta$ -dibromostyryl derivative, which was prepared in high yield, 85%. The  $\beta,\beta$ -dibromostyryl derivative then undergoes the low temperature reaction with BuLi, followed by quenching of the acetylide with DMF and subsequent acid hydrolysis. This reaction proved unsuccessful and the desired product was not isolated from the reaction mixture. The effect of the 4-nitro- withdrawing group has a destabilising effect on the intermediate and results in no product formation.

It was decided to try and synthesise the 4-nitrophenylpropynal from the palladium catalysed reaction of 4-iodonitrobenzene and propiolaldehyde diethyl acetal, followed by acid hydrolysis to yield the desired aldehyde.



- i) copper II iodide, Bis(triphenylphosphine)palladium chloride, triethylamine:
- ii) H<sup>+</sup>/H<sub>2</sub>O/DMSO.

The palladium catalysed reaction of 4-iodonitrobenzene with propiolaldehyde diethyl acetal was carried out in dry triethylamine, under nitrogen and was complete within five minutes. On addition of the propiolaldehyde diethyl acetal to a mixture of 4-iodonitrobenzene, copper (II) iodide and bis (triphenyl phosphine) palladium (II) chloride, a brown precipitate resulted almost immediately. This was extracted from the mixture with diethylether and subjected to column chromatography to yield the desired diacetal as a yellow

oil in 87% yield. The 4-nitrophenylethyndiethylacetal was characterised by  $^1\text{H}$  nmr and mass spectrometry. The diacetal is then added to a mixture of concentrated sulphuric acid, water and dimethylsulphoxide and heated to  $95^\circ\text{C}$  for thirty minutes. The reaction mixture was added to a saturated solution of ammonium chloride and the product extracted with diethylether and subjected to column chromatography. This yielded the desired 4-nitrophenylpropynal as a yellow solid in approximately 50% yield. This was confirmed by mass spectrometry with the molecular ion at  $m/z - 175$  being the base peak. The fragmentation pattern is also consistent with a nitrophenyl aldehyde with peaks for the loss of  $\text{HCO}^+$  ion, the loss of the  $\text{NO}^+$  ion and for the loss of  $[(\text{NO}_2)^+ - (\text{C}_3\text{HO})^+]$  ion all being confirmed. The  $^1\text{H}$  nmr also showed the formation of the arylethynyl aldehyde but this was confirmed beyond doubt from the infrared spectrum with characteristic stretches for the acetylene at  $2194\text{ cm}^{-1}$ , the aldehyde  $\text{C}=\text{O}$  stretch at  $1658\text{ cm}^{-1}$  and the  $\text{NO}_2$  stretches at  $1518$  and  $1344\text{ cm}^{-1}$ .

The synthesis of the meso-5,15-bis-(4-dodecyloxyphenylethynyl)-10,20-bis-(4-nitrophenylethynyl) porphyrin was then attempted using the Lee and Lindsey<sup>(24)</sup> two-pot procedure, reacting 4-dodecyloxyphenylethynyl dipyrromethane with 4-nitrophenyl propynal with a  $\text{BF}_3 \cdot \text{OEt}_2$  catalyst at  $-25^\circ\text{C}$ . The procedure is the same as described earlier, the aldehyde and dipyrromethane are dissolved in DCM, degassed with nitrogen, the reaction temperature reduced to  $-25^\circ\text{C}$  and the catalyst added. Upon oxidative work-up with DDQ, the characteristic green colour associated with the tetra-arylethynyl porphyrins in DCM was observed. Preliminary UV/visible studies confirmed the formation of a tetraarylethynyl porphyrin had been achieved with the characteristic red shift to  $478\text{ nm}$ . The porphyrin mixture was subjected to column chromatography on silica gel and a number of porphyrin green bands were observed. The main band eluted from the column was concentrated by evaporation and characterisation analysis performed. Uv/visible spectroscopy indicated that the porphyrin had been synthesised with a slight bathochromic shift of the B band some  $5\text{ nm}$  on introduction of the 4-nitro groups. Infrared spectroscopy

indicated the isolation of ethynyl porphyrin with alkoxy and nitro groups present. The ethynyl stretches can be observed at  $2325\text{ cm}^{-1}$  and  $2105\text{ cm}^{-1}$ , the nitro stretches at  $1450\text{ cm}^{-1}$  and  $1350\text{ cm}^{-1}$  and the alkoxy stretch at  $1075\text{ cm}^{-1}$ . The rest of the techniques;  $^1\text{H}$  nmr, mass spectrometry and microanalysis used to identify the correct structure of compounds, however indicated that we had not synthesised the desired porphyrin.

The  $^1\text{H}$ nmr spectrum of a 5,15-bis-10,20-porphyrin would have a characteristic AB spin quartet for the  $\beta$ -pyrrolic-protons. On inspection of the  $^1\text{H}$ nmr spectra of the isolated product, there are more AB spin quartets present than expected. The mass spectrum for the compound shows no expected ion peaks and also shows mass peaks greater than that of the expected molecular ion. The microanalysis data of the compound shows that the percentage of carbon is higher than expected and that of nitrogen is lower. Inspection of all the data for this compound suggests that the porphyrin macrocycle incorporates both the arylolethynyl groups, but not in the expected form of the 5,15-bis-10,20 porphyrin as expected. The fact that the microanalysis shows a lower nitrogen value and higher carbon value than expected, indicates there is more of the alkoxy derivative and less of the nitro derivative substituted in the porphyrin periphery. This could also be used to explain why there are more AB spin quartets in the  $^1\text{H}$  nmr spectrum than expected.

In the synthesis of the desired bis-porphyrin, there seems to be a rearrangement of meso-substituents to yield the 5,10,15-tris-(4-dodecyloxyphenylethynyl)-20-(4-nitrophenylethynyl) porphyrin (Figure 4.12). There appears to be a scrambling effect in operation, whereby one 4-nitro-phenylethynyl group is replaced by that of a 4-dodecyloxyphenylethynyl group.

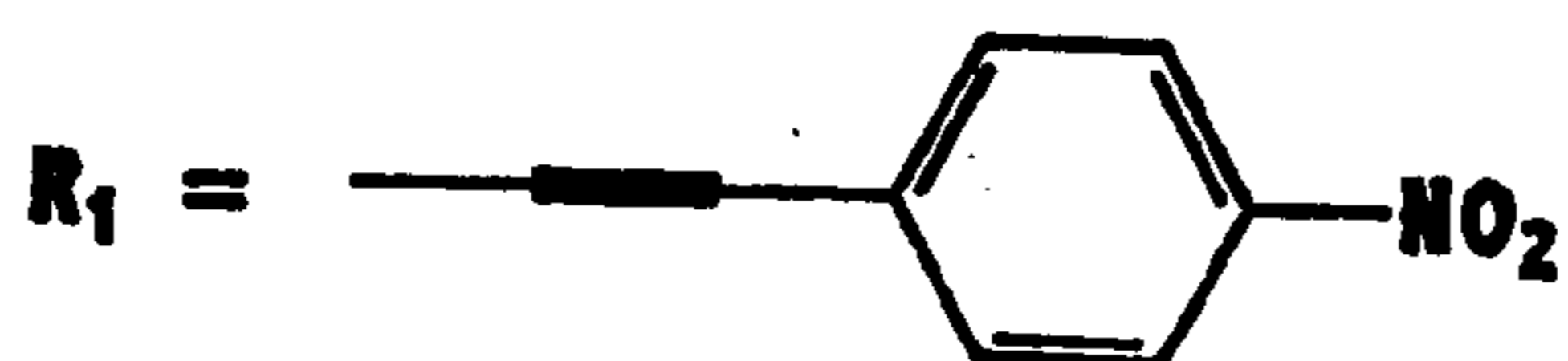
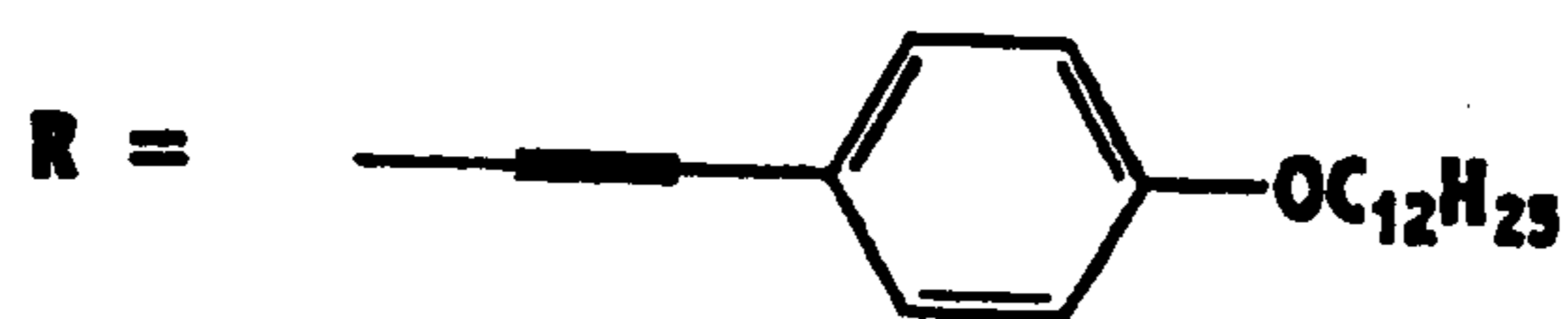
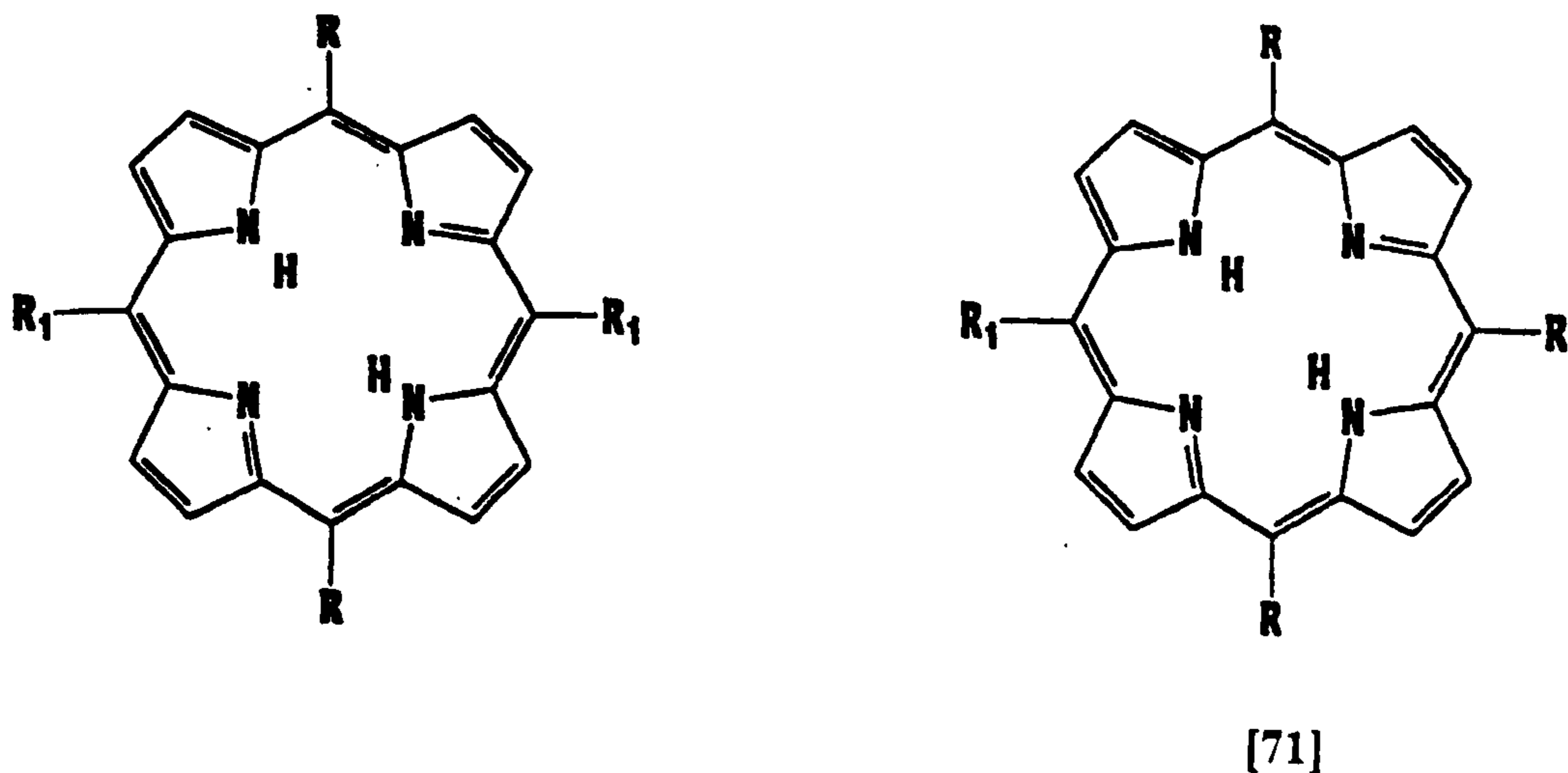


Figure 4.12

The scrambling effect can be used to explain why the UV/visible spectra appears normal in that the four arylethynyl groups contribute to the position of the B band and that the ir spectrum shows that both groups are present. The inclusion of the third dodecyloxy group can explain why there are mass peaks greater than the expected molecular ion peak, the percentage of nitrogen and carbon vary so much and the observation of more AB spin quartets than expected in the  $^1\text{Hnmr}$ .

On closer inspection of the  $^1\text{H}$  nmr spectrum it is evident that there are five AB spin quartets observable. This strengthens the idea that there are three dodecyloxy-groups and one nitro-group in the macrocycle as this introduces a

degree of unsymmetricality to the system which will cause more splitting in the  $^1\text{H}$  nmr spectrum.

The first noticeable effect of the introduction of the electron withdrawing group is the upfield shifts of the proton resonances. The  $\beta$ -pyrrolic resonances for the protons  $\text{H}_c$ ,  $\text{H}_d$  have shifted from 9.13 ppm  $\rightarrow$  8.3 ppm and  $\beta$ -pyrrolic resonances for the protons  $\text{H}_a$ ,  $\text{H}_b$  from 9.13 ppm  $\rightarrow$  7.5 ppm. The decrease in the electron density of  $\pi$ -system diminishes the ring current and may cause upfield proton shifts. This is the opposite effect where a decrease in electron density generally leads to a reduced shielding effect and hence downfield shifts. The  $\beta$ -pyrrolic resonances are observed as two AB spin quartets at resonances 8.41, 8.40, 8.26, 8.25 and 7.86, 7.84, 7.23, 7.21. The introduction of the nitro-group has the effect of introducing three different environments for the phenyl protons and this is the reason for the additional AB spin quartets in the spectrum.

The phenyl protons on the  $\text{C}_5$  and  $\text{C}_{15}$  meso positions will be in the same environment, but different to those of  $\text{C}_{10}$  which is different again to that of  $\text{C}_{20}$ . This is observed in the  $^1\text{H}$  nmr spectrum with the three AB spin systems in the ratio 1:1:2 in terms of the number of protons. In comparison to the symmetrical (4-dodecyloxyphenylethynyl) porphyrin these phenyl proton resonances have shifted upfield from 7.91, 7.89, 7.06, 7.04  $\rightarrow$  7.46, 6.44, 6.79, 6.77. Another indication that the tri-dodecyl derivative has been produced is that the proton resonances for the  $-\text{CH}_2$  protons next to the oxygen group are now in two different environments and this is observed in the  $^1\text{H}$  nmr spectrum. The mass spectrum indicates the formation of the 5,10,15-tris(4-dodecyloxyphenylethynyl)-20-(4-nitrophenylethynyl) porphyrin by mass peaks of the loss of  $\text{NO}_2^+$  at  $m/z = 1263$ , the loss of one R group at  $m/z = 1024$  and the loss of one R and  $\text{R}_1$  group at  $m/z = 880$ . The final confirmation that this was the isolated porphyrin was the microanalysis. As already mentioned, the lower nitrogen percentage and higher carbon percentage is consistent with the newly proposed structure.

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## 5 RESULTS AND DISCUSSION :

### Nonlinear Absorption Results

There are several techniques known for the measurements of nonlinear refraction in materials <sup>(1,6)</sup>. These methods are sensitive techniques but require complex experimental apparatus. An alternative method was presented by Said et al <sup>(7)</sup> based on the principles of spatial beam distortion, enabling a single-beam technique for measuring the sign and magnitude of refractive nonlinearities. The technique known as the Z-scan, has been employed on several materials in the IR and the visible regions, and the nonlinearities measured with nano- and picosecond pulses.

A simplification of the Z-scan experimental apparatus is shown in Figure 5.1.

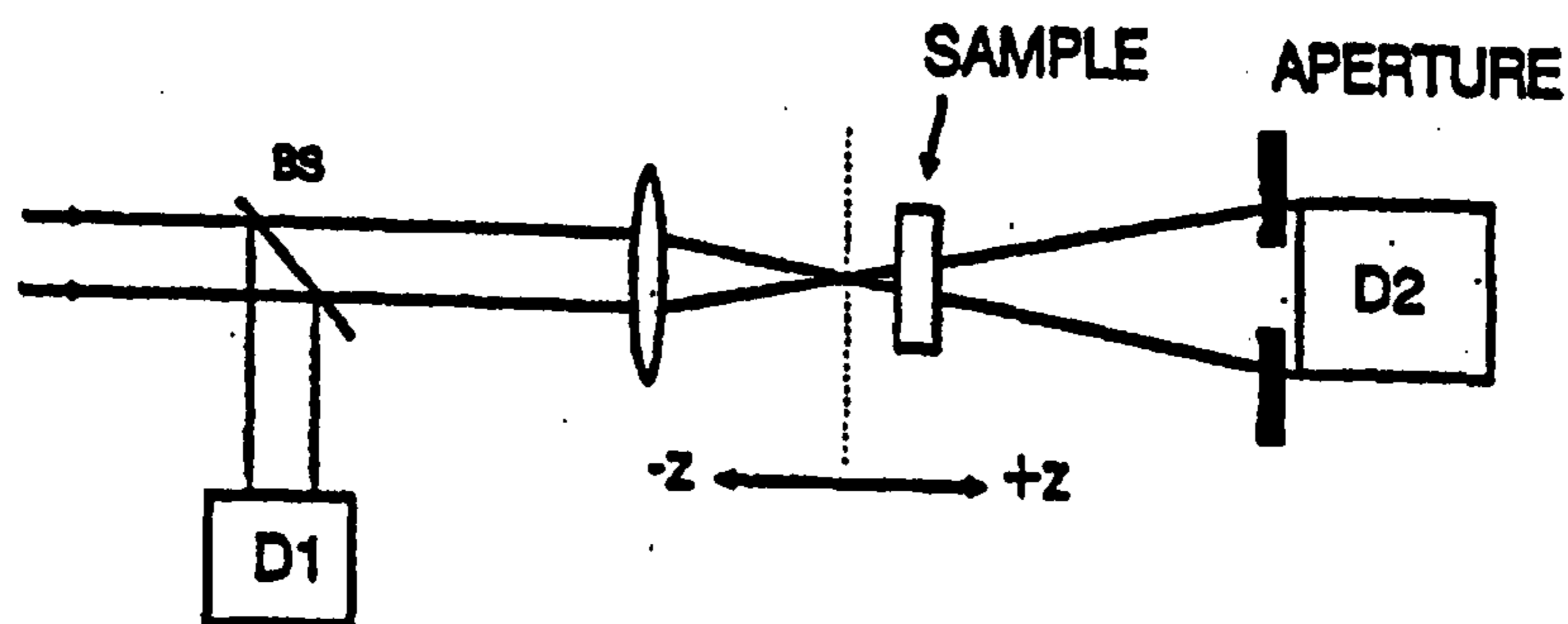


Figure 5.1. Z-scan experimental apparatus.

The method consists of bringing a laser beam to a focus and moving a thin sample along the optical axis in the Z direction, while keeping the energy of the laser beam constant. Using a Gaussian laser beam the transmittance of a nonlinear medium is measured through a finite aperture. After the beam passes through the sample it is detected by a calibrated silicon detector. All the transmitted light is detected in an open aperture configuration in an attempt to reduce complications of nonlinear refraction affecting the measurement of



reduce complications of nonlinear refraction affecting the measurement of nonlinear absorption. The transmission is measured for a number of Z positions through the focus. In order to eliminate surface damage effects, it is necessary to translate the sample through the focus in one direction and then back in the reverse direction.

A typical Z-scan shows three different regions of absorption.

- (1) far from the focus linear absorption is observed.
- (2) closer to the focus an induced absorption occurs and,
- (3) at the focus, saturation of the absorption is observed.

We can now measure the difference  $\Delta T$  between the normalised peak (maximum) and valley (minimum) transmittances as a screening test to give the sign, magnitude and order of the nonlinear response of new nonlinear optical materials.

For our purposes, a series of porphyrin macrocycles were screened (courtesy of DERA, Malvern), to identify if they had any nonlinear optical properties. This was simply achieved by measuring the difference between the maximum and the minimum, which is represented as the linear transmission and the nonlinear transmission. As a screening process, and for simplicity, the material is considered to be a useful nonlinear optical material, if the difference  $\Delta T$  is large. Having a large  $\Delta T$  doesn't necessarily mean that the material will show suitable RSA properties unless the linear transmission is also large to start with. A combination of a high linear transmission and a large  $\Delta T$  make for a potentially useful nonlinear optical material.

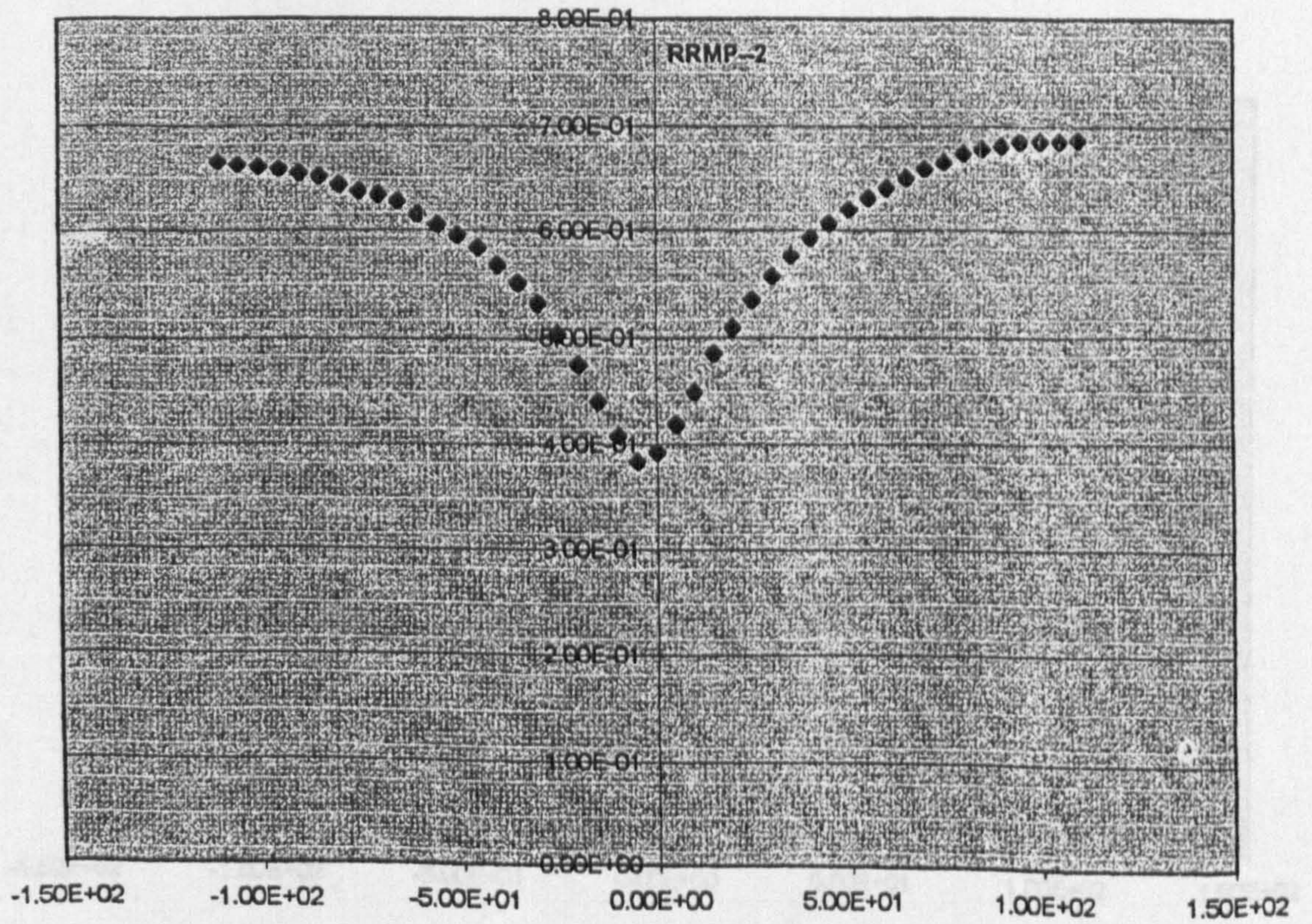
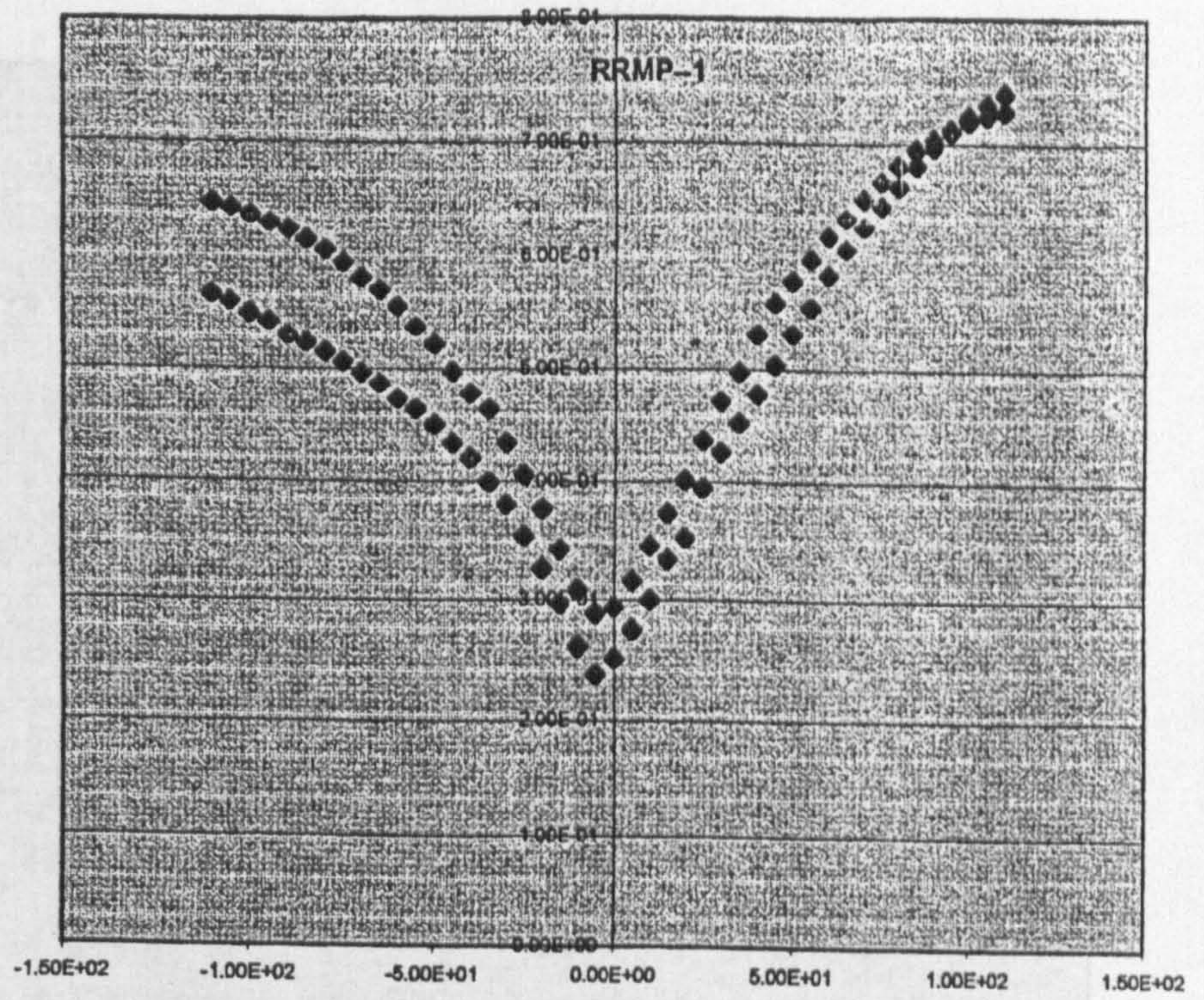
The synthesis of a series of substituted porphyrin compounds have already been reported, and solutions of the porphyrins in dichloromethane were subjected to the Z-scan technique to measure their nonlinear susceptibility. The results are represented in Table 5.1 for the porphyrin compounds at several wavelengths throughout the visible region. The normalised transmittance graphs for the porphyrins are also included in Figures 1- 30.

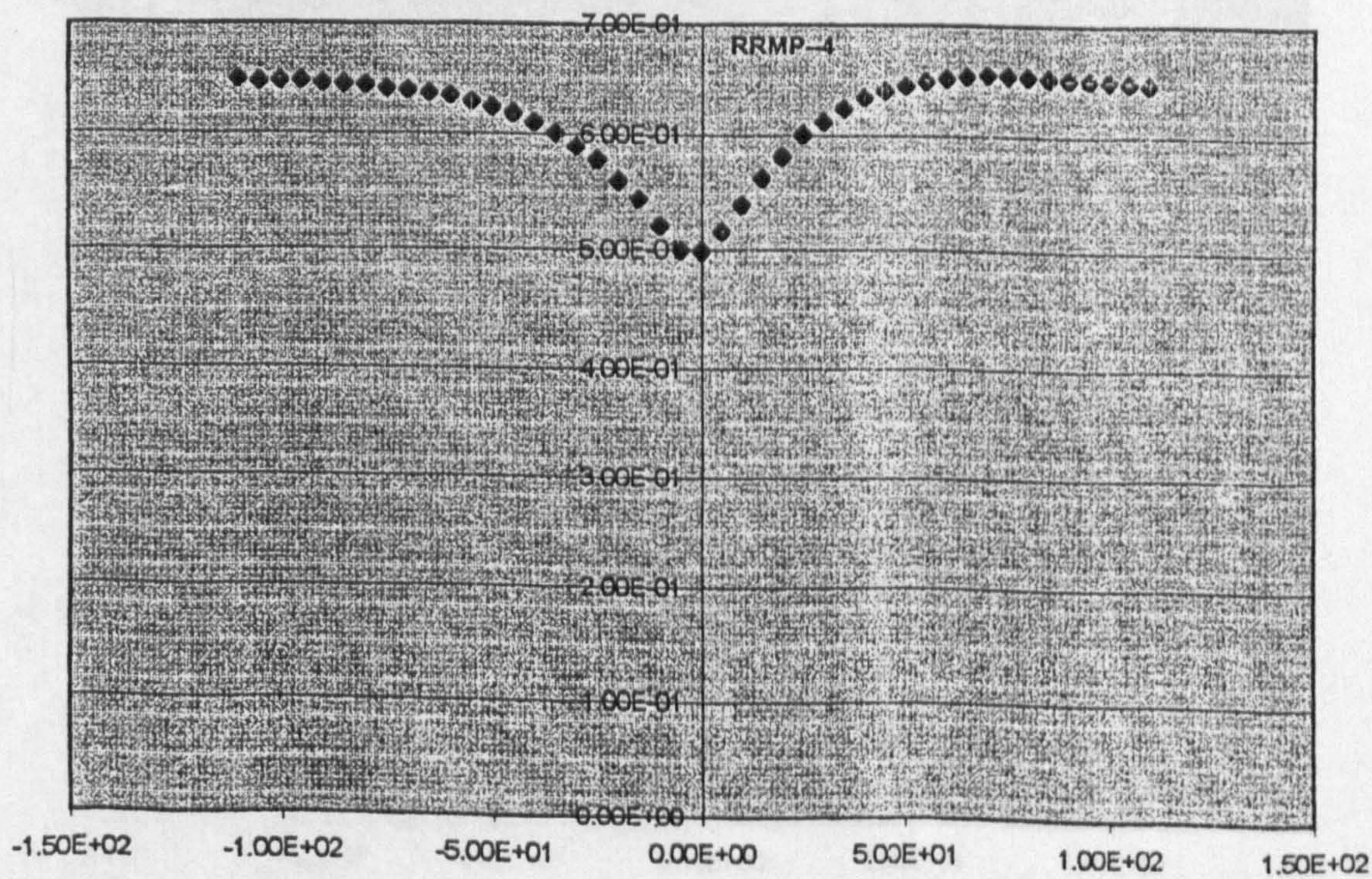
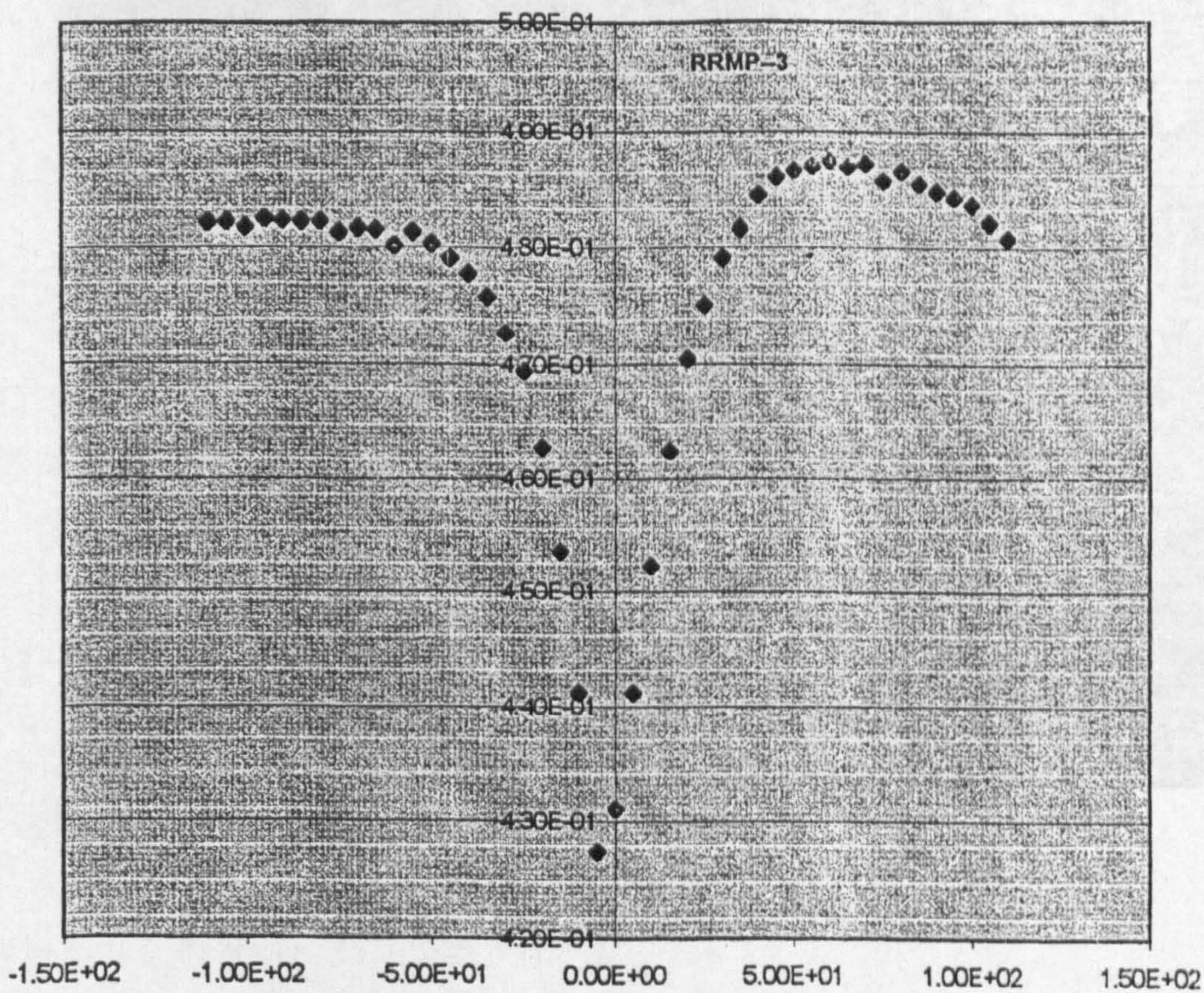
<b>Porphyrin</b>	<b>Wavelength (<math>\lambda</math>)</b>	<b>% Linear Transmittance</b>	<b>% Non-linear Transmittance</b>	<b><math>\Delta T</math></b>
MP	450	74.1	23.8	50.3
	500	68.8	38.4	30.4
	520	48.1	42.7	5.4
	540	64.6	49.9	14.7
	580	70.3	59.4	10.9
	625	80.9	71.3	9.6
MMP	500	73.7	56.3	17.4
	500	71.1	62.7	8.4
	525	77.0	66.9	10.1
	550	81.1	74.6	6.5
NMP	540	76.0	64.0	12.0
	500	64.2	51.4	12.8
	600	68.5	68.5	
DMP	520	71.6	70.4	1.2
	550	74.6	74.7	
DNOP	500	50.5	67.6	
	640	89.0	85.7	3.3
	600	76.5	74.7	1.8
	430	74.9	75.1	
TNOP	600	67.4	45.0	22.4
	500	2.0	18.3	
	430	27.5	31.1	
	640	88.3	86.0	2.3
TXOP	640	90.0	89.5	0.5
	500	55.5	74.4	
	430	80.2	80.2	
	530	83.0	61.6	21.4
TEP	530	82.7	61.9	20.8
	590	77.0	70.0	7.0
	566	82.6	67.6	15.0
	503	72.4	51.7	20.7
	532	55.23	24.78	30.45
TPEP	500	39.23	16.20	23.03
	532	62.06	4.6	57.46
MBrEP	500	39.21	0.86	38.35
	510	25.6	12.9	12.7
TNEP	532	50.86	16.9	33.96
	550	56.44	25.2	31.24

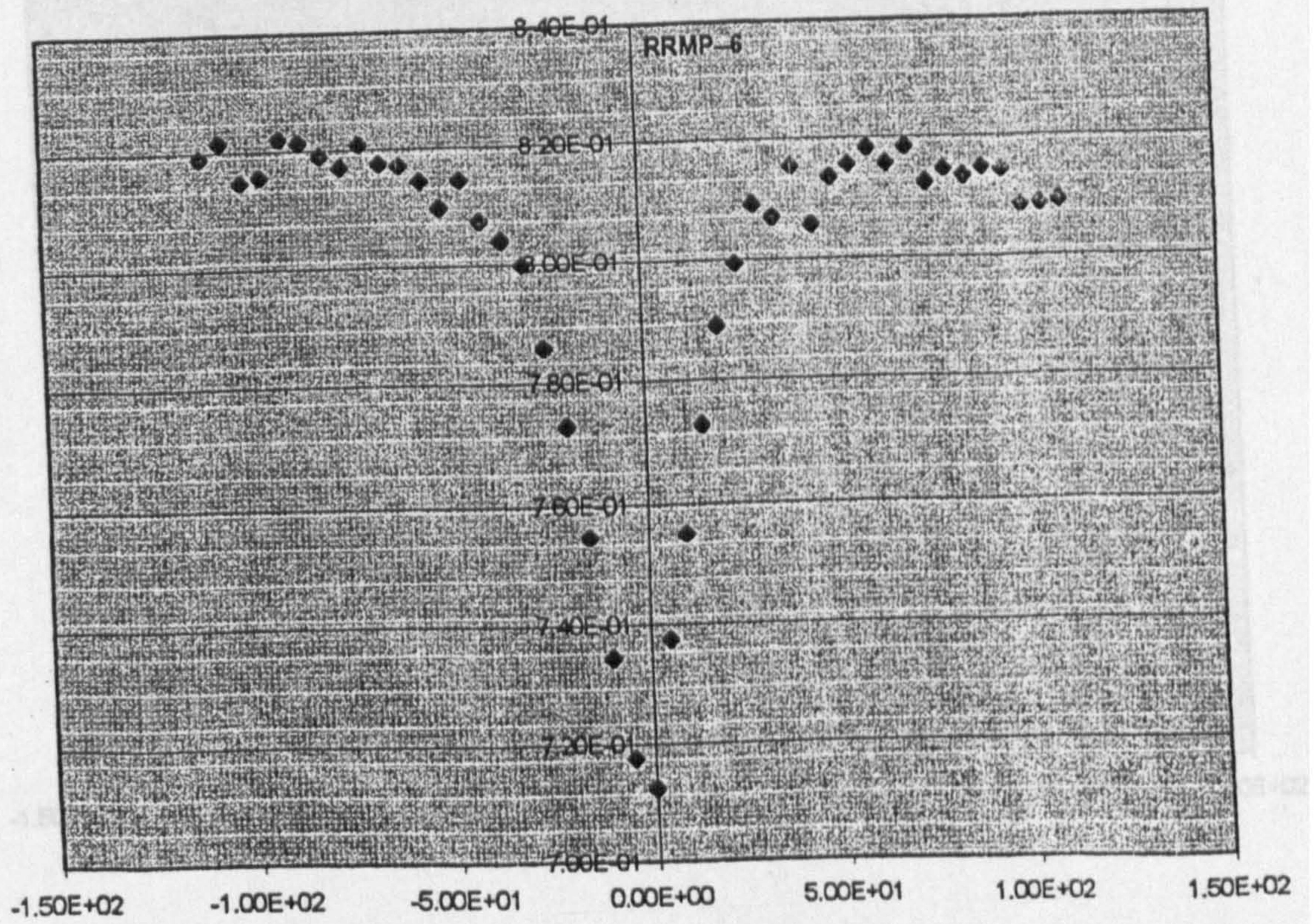
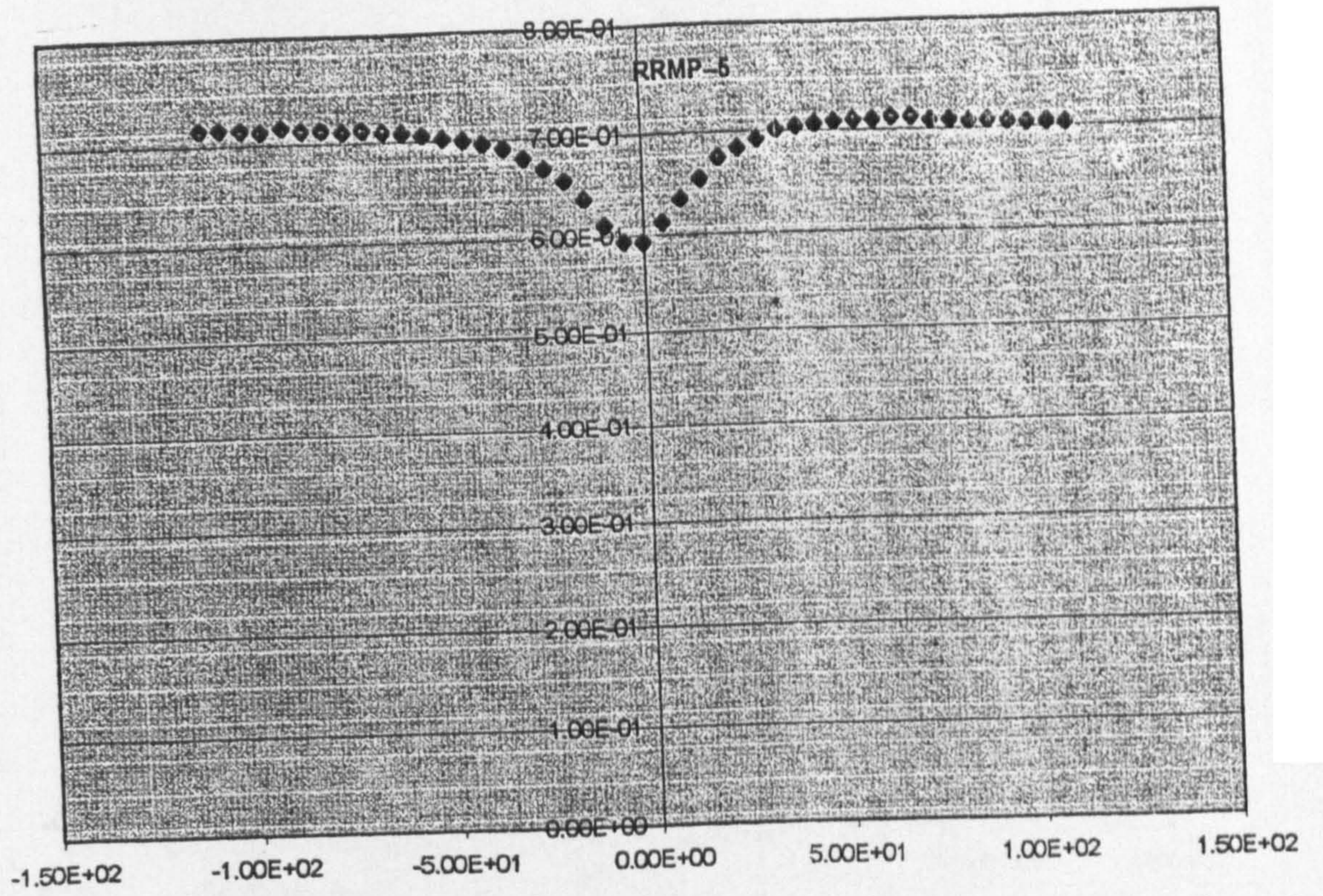
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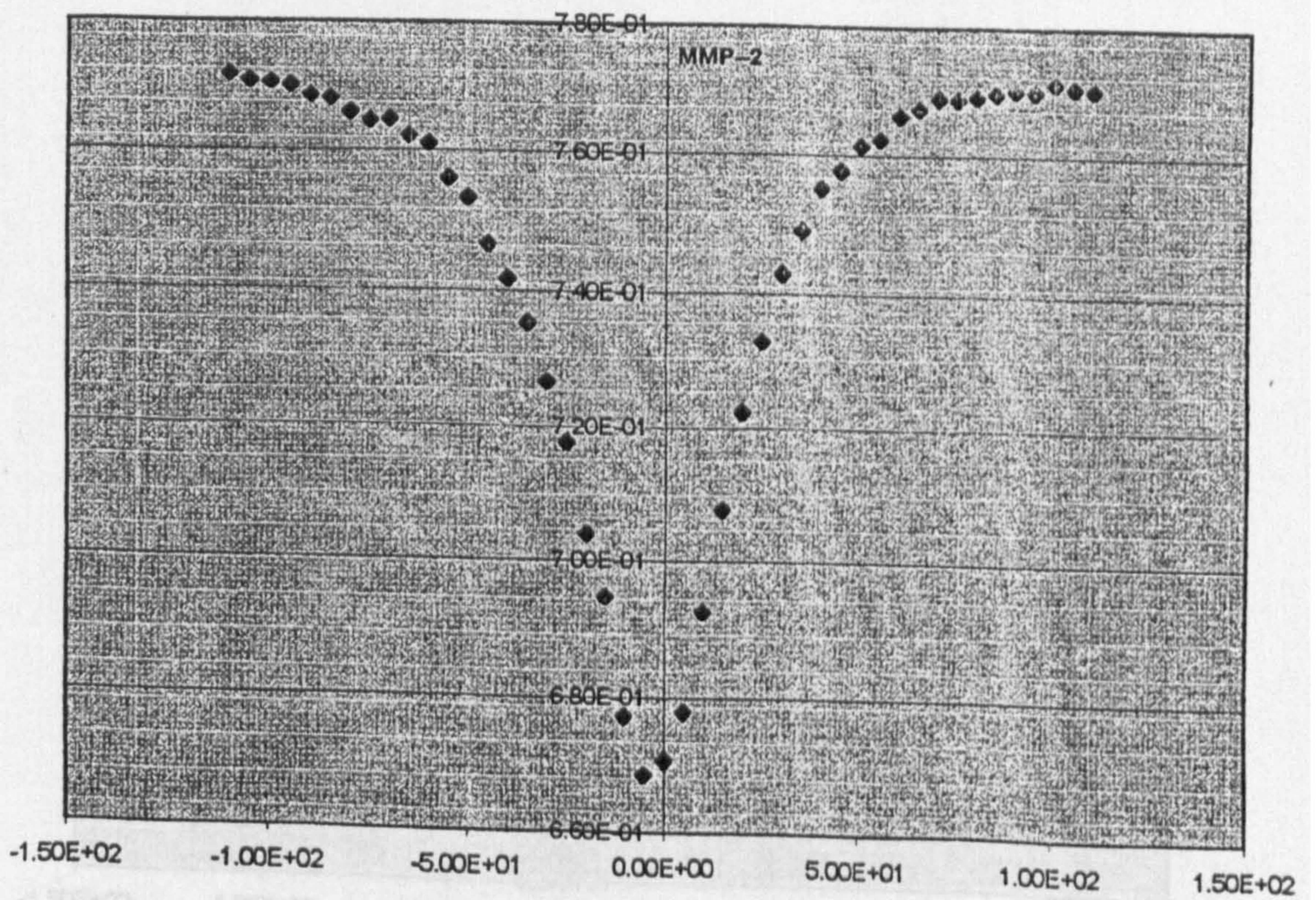
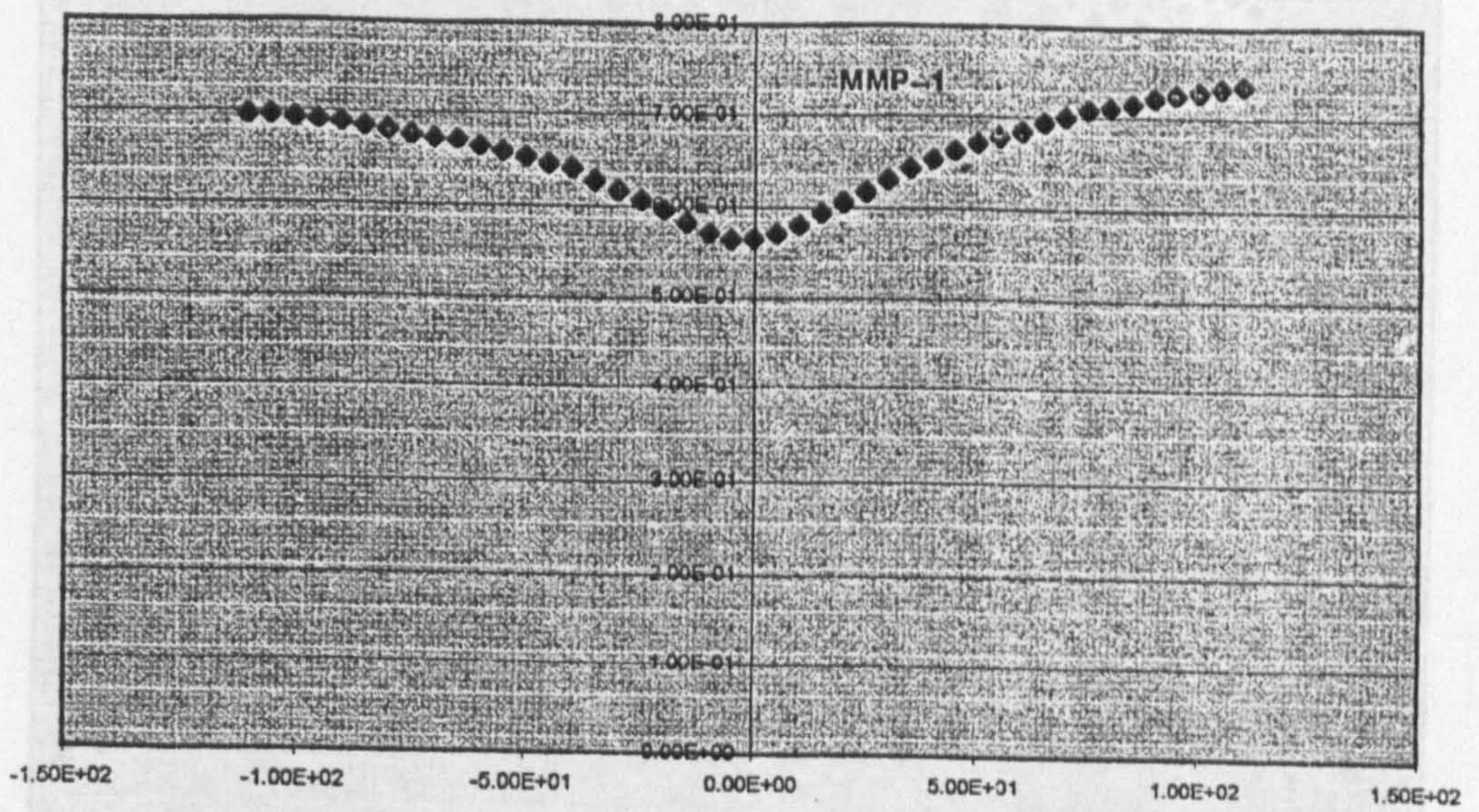
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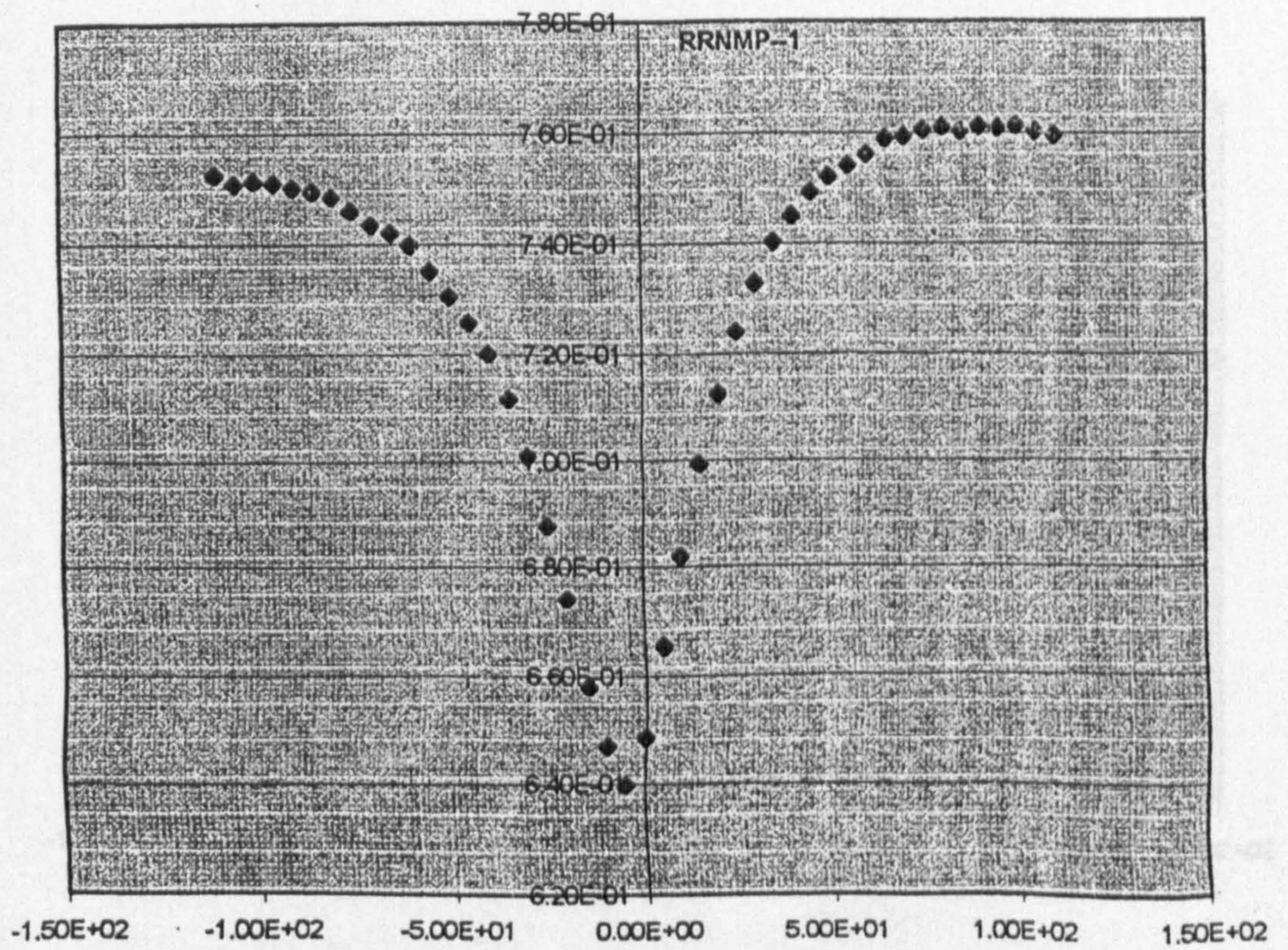
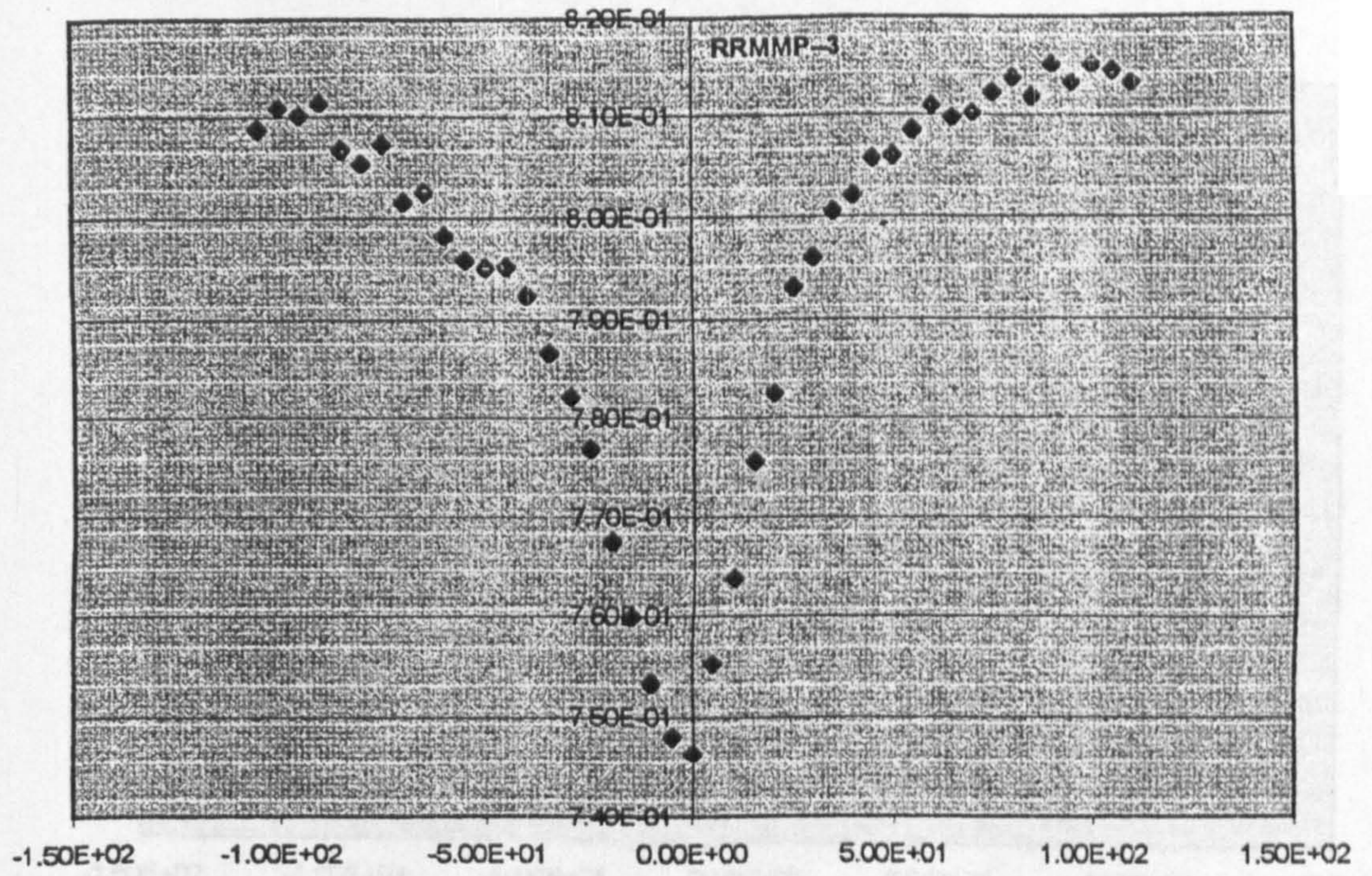
Table 5.1

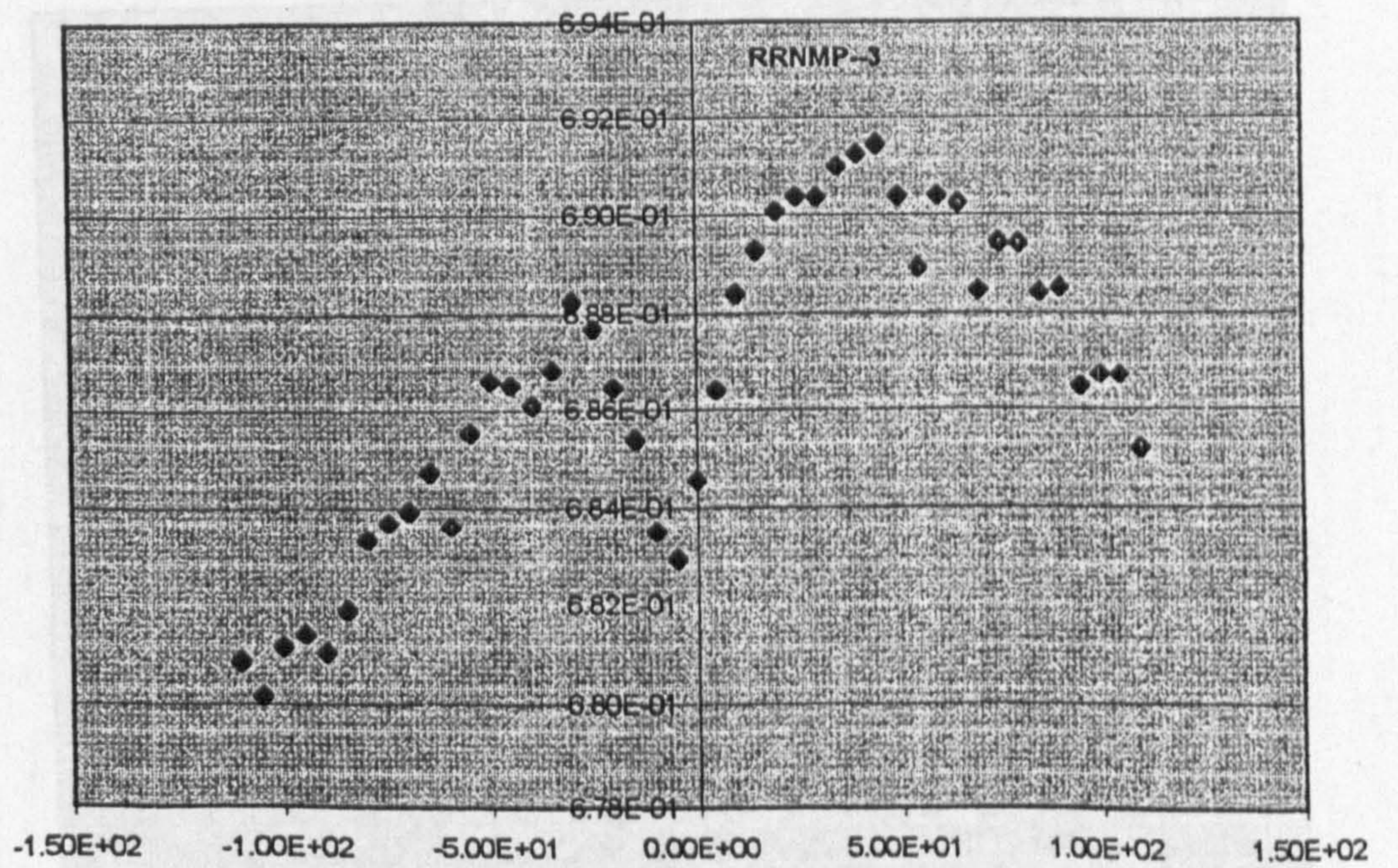
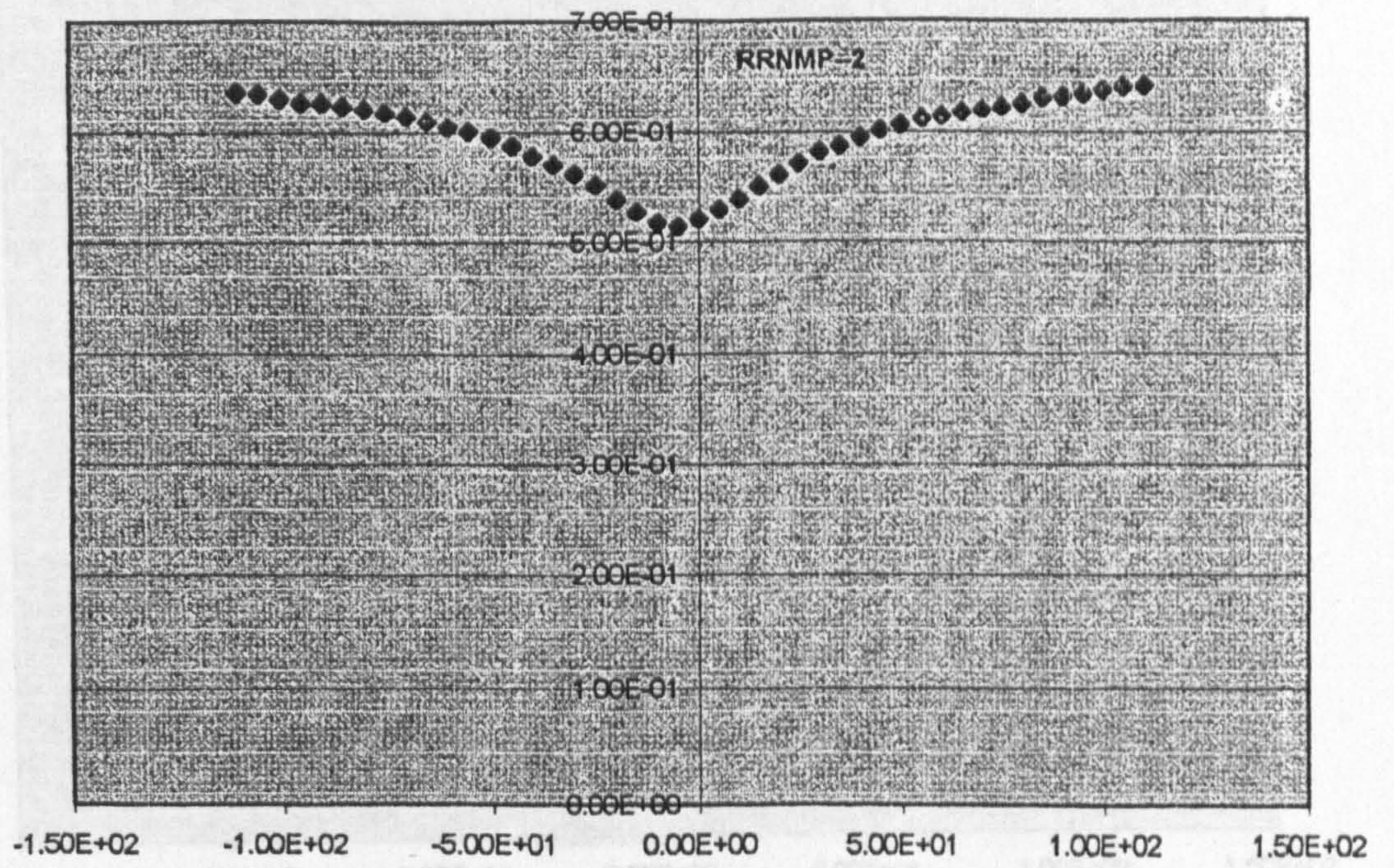




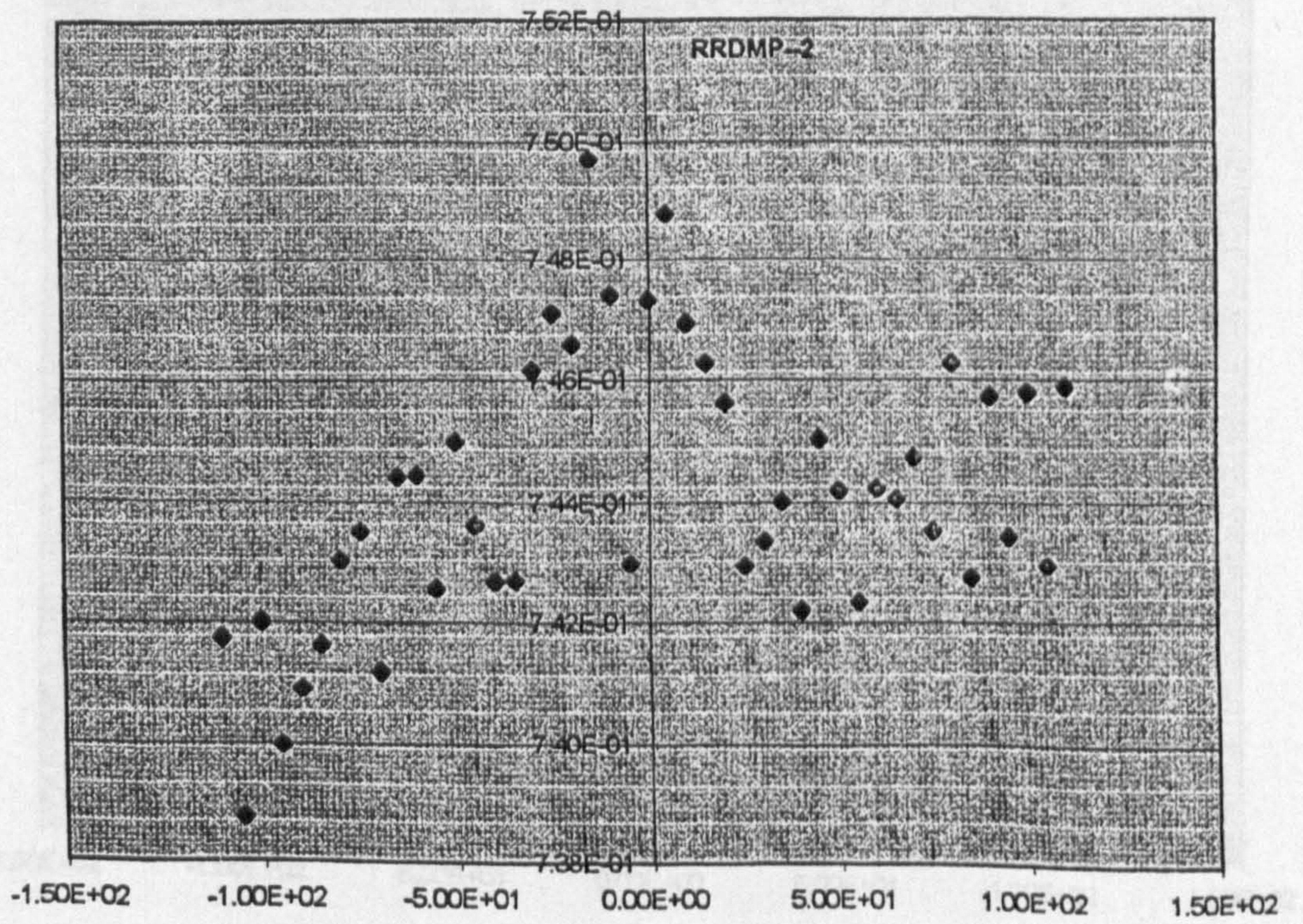
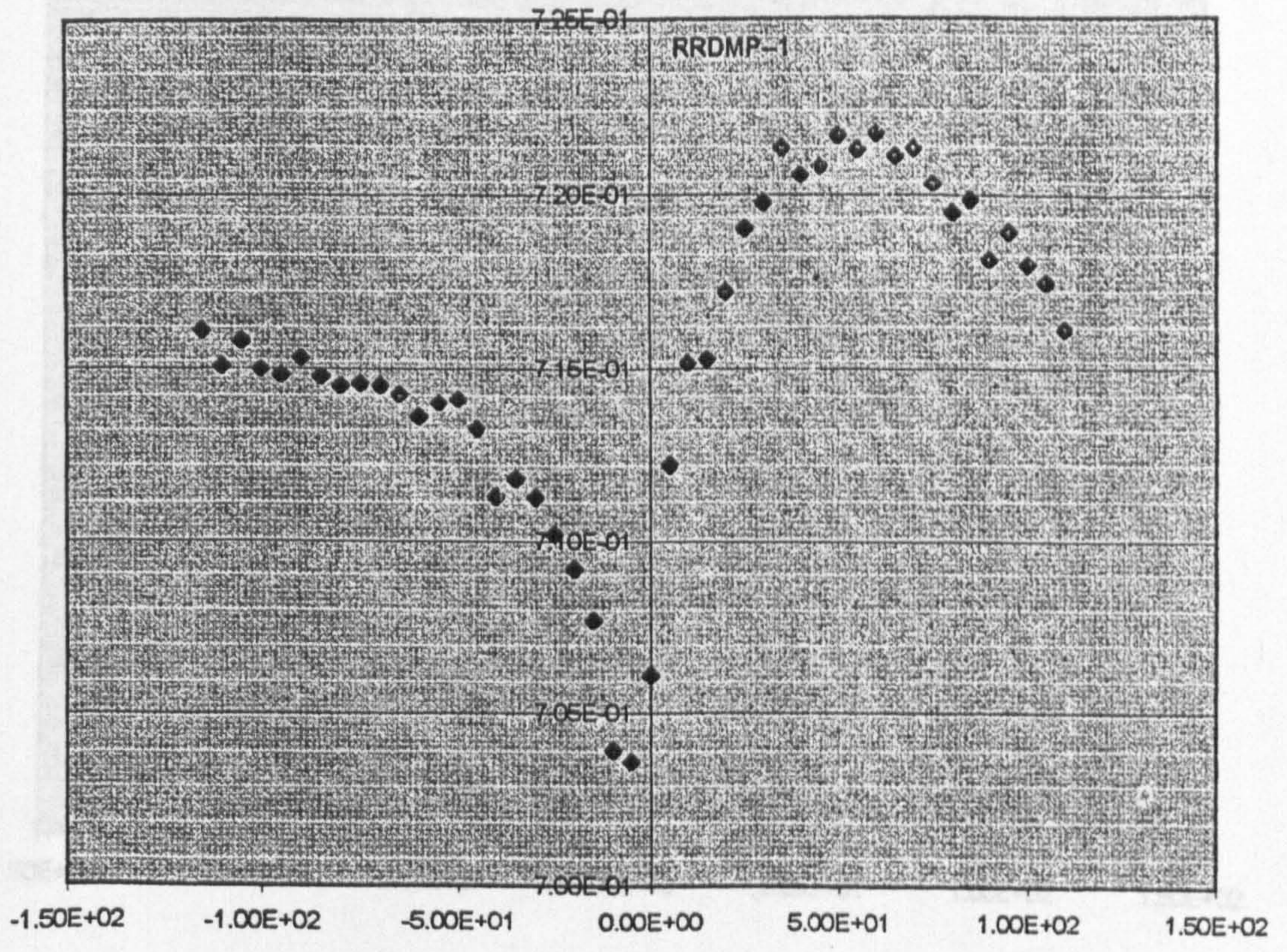


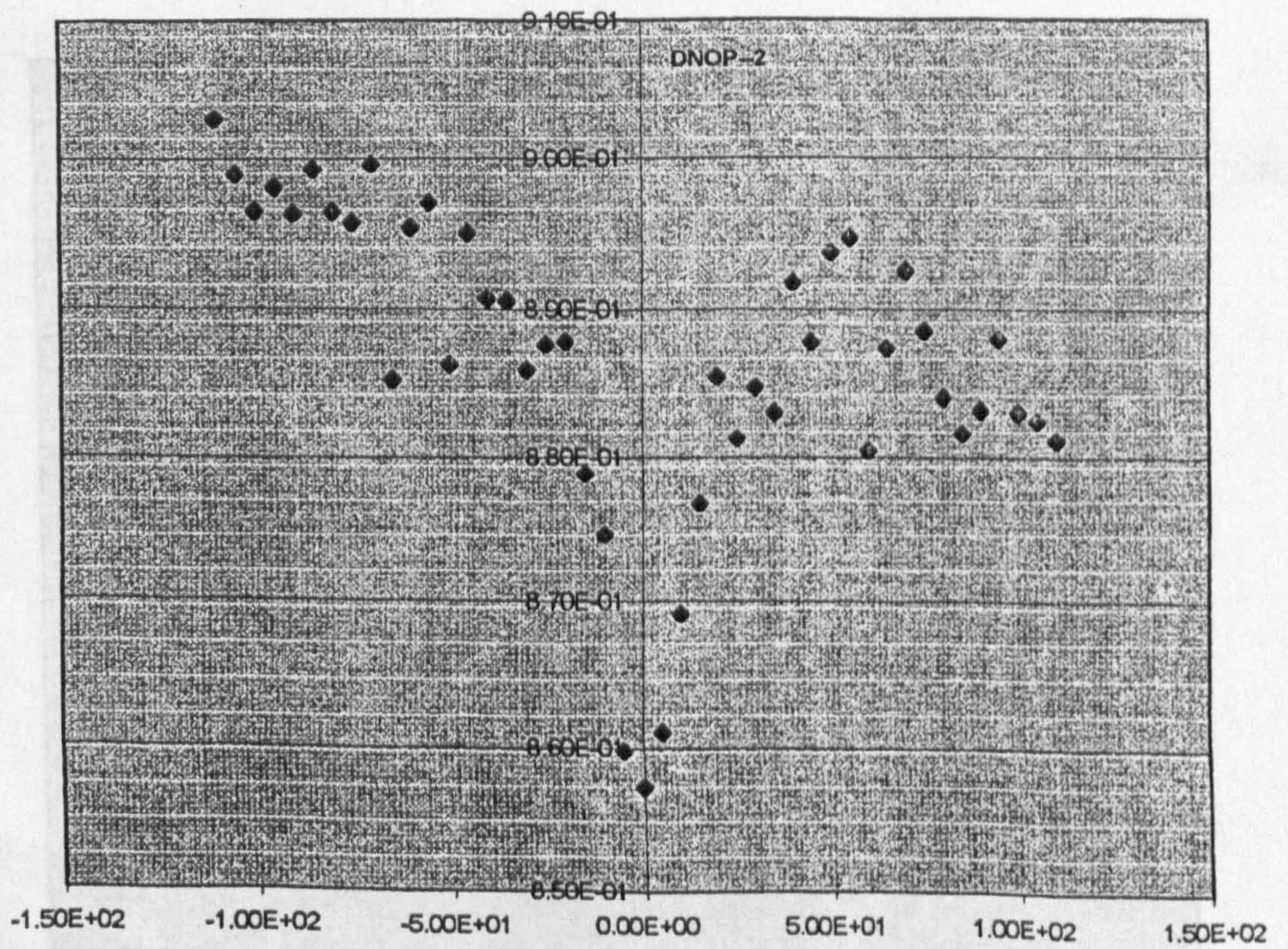
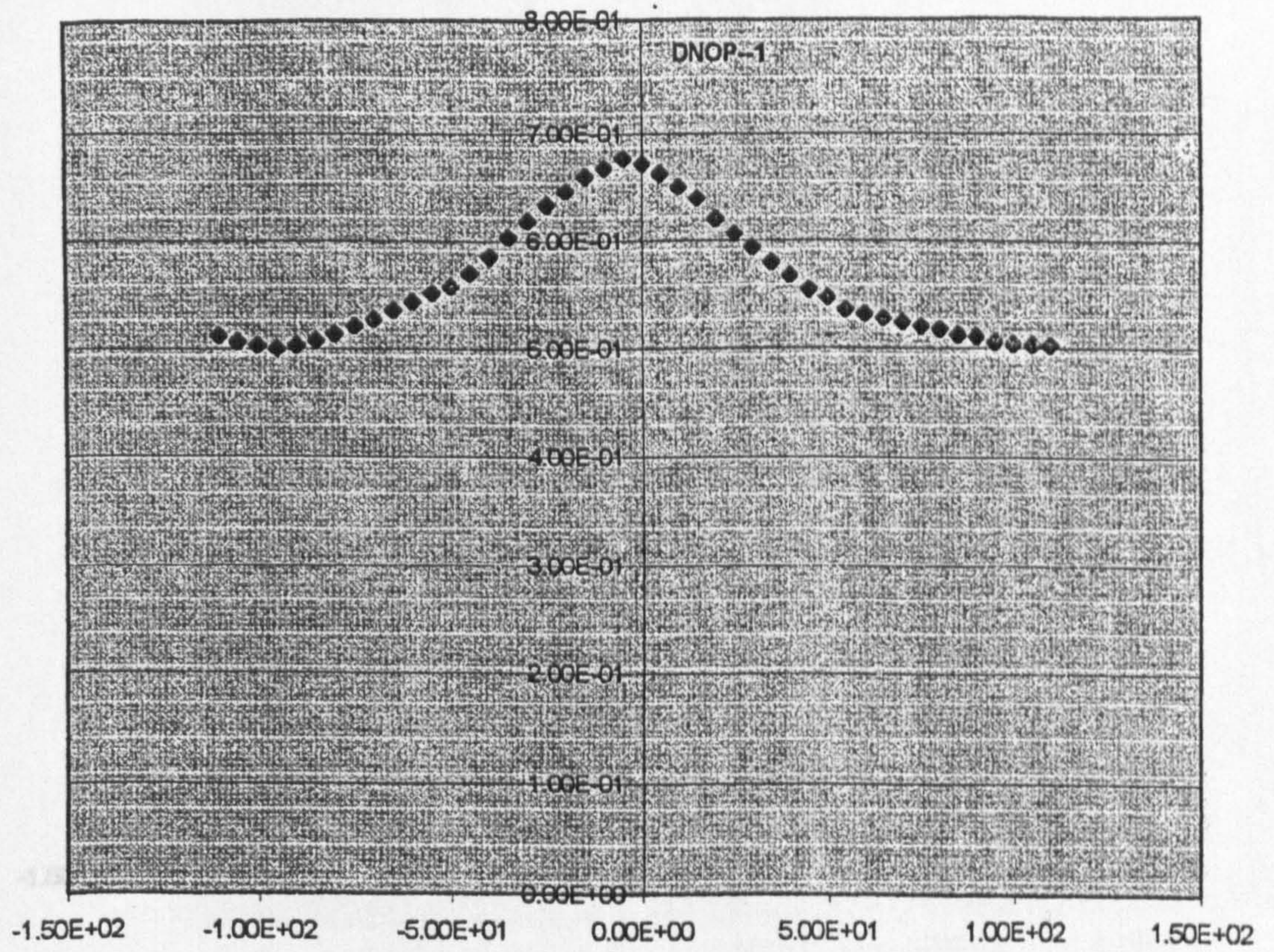


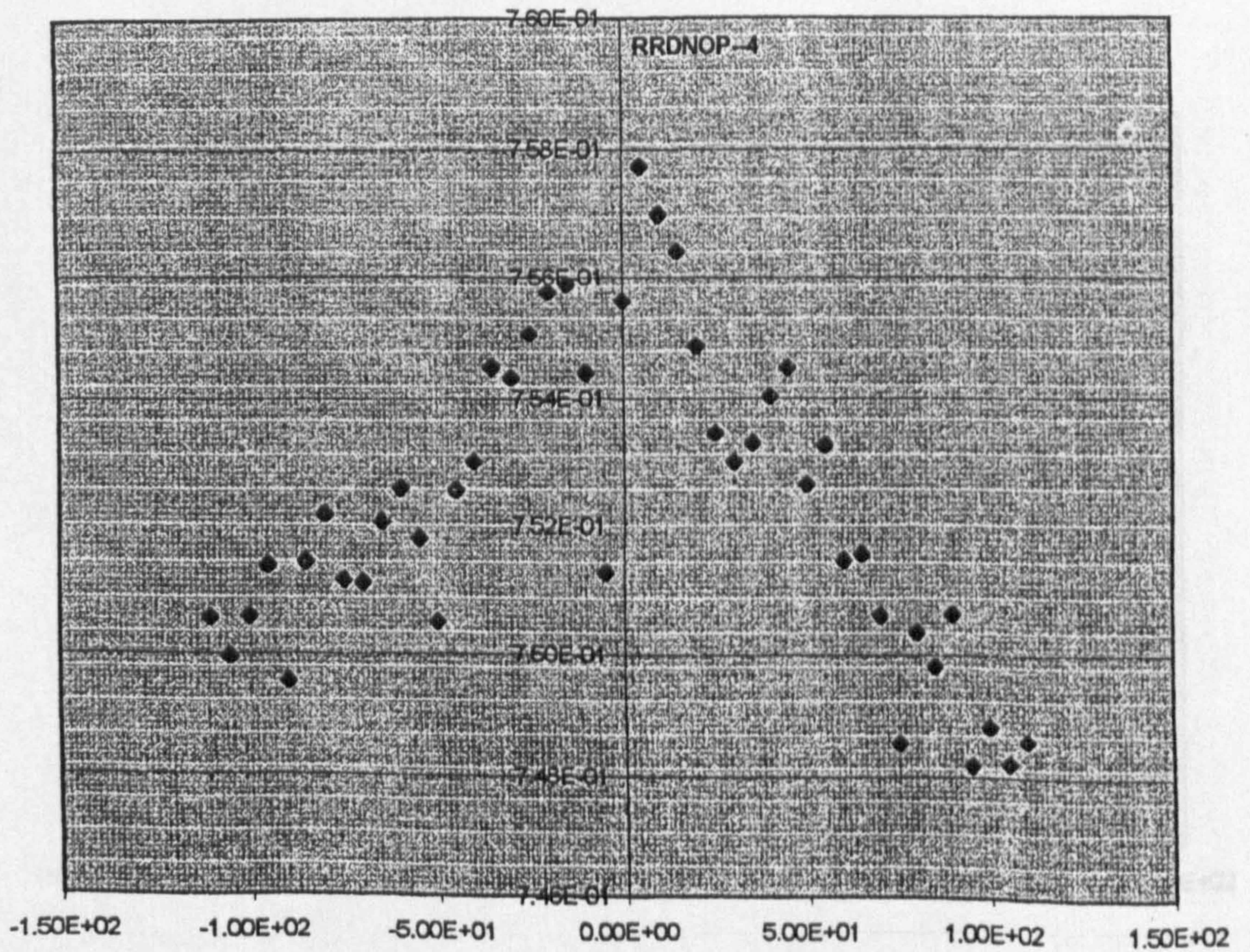
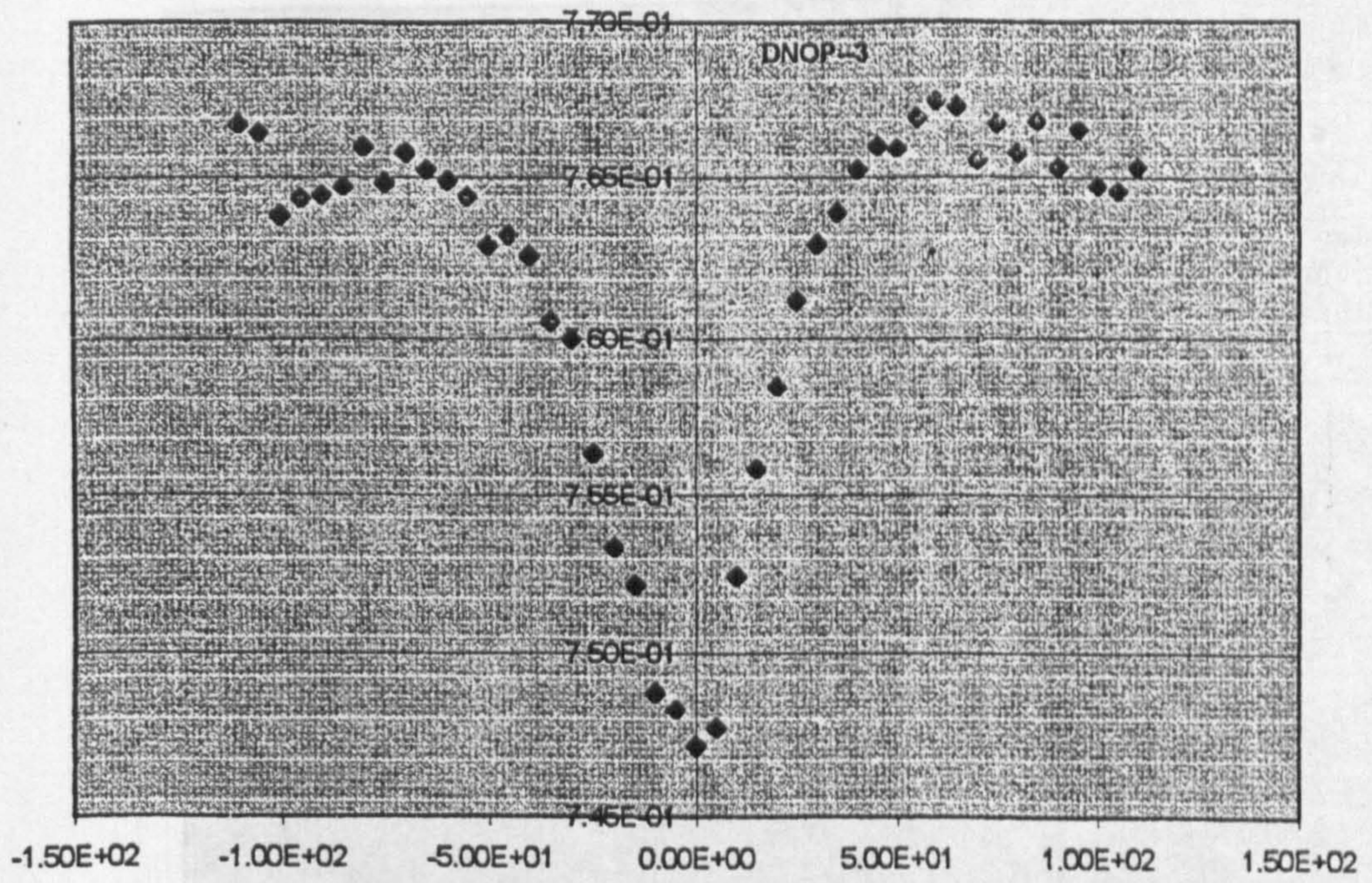


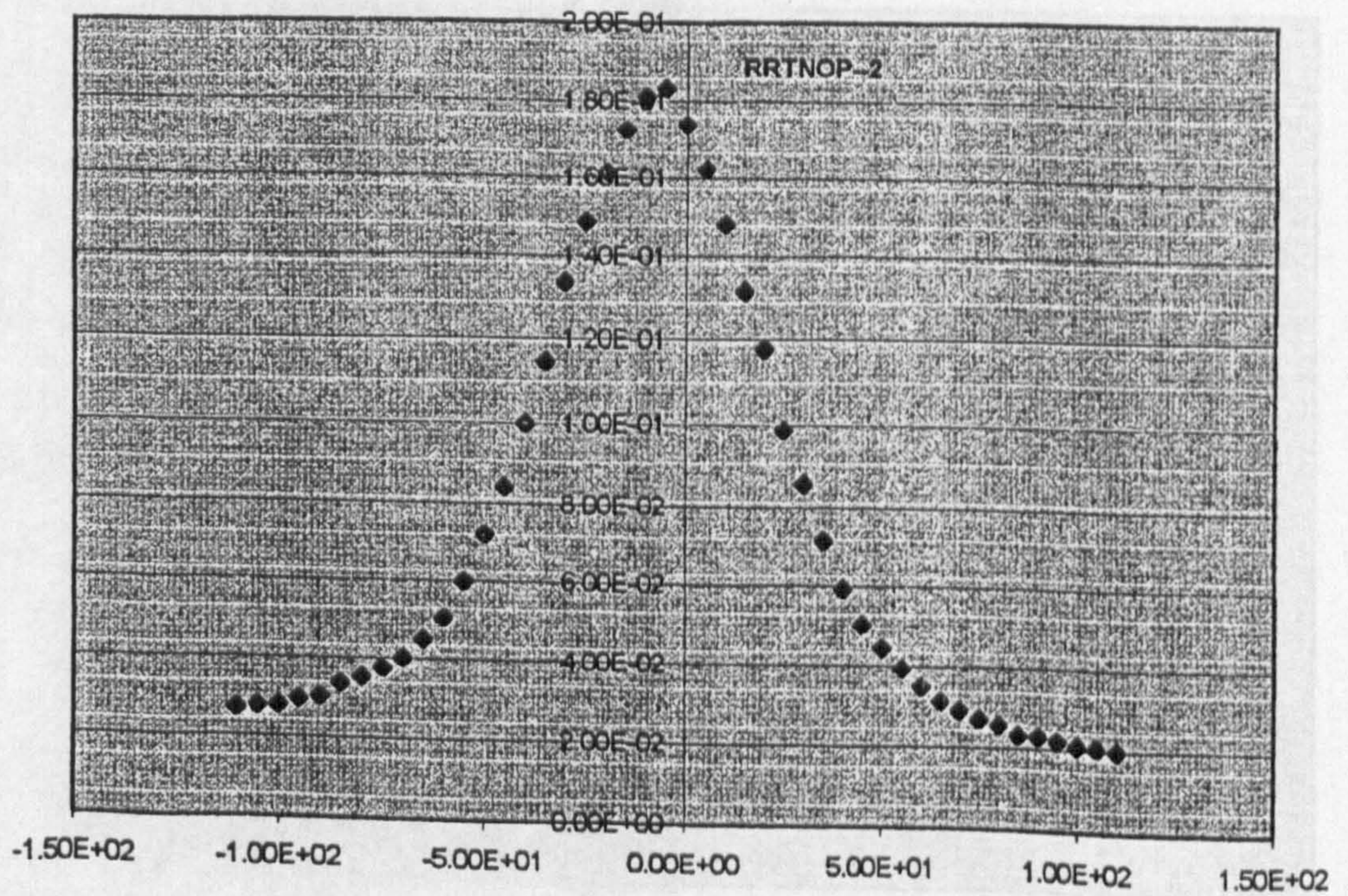
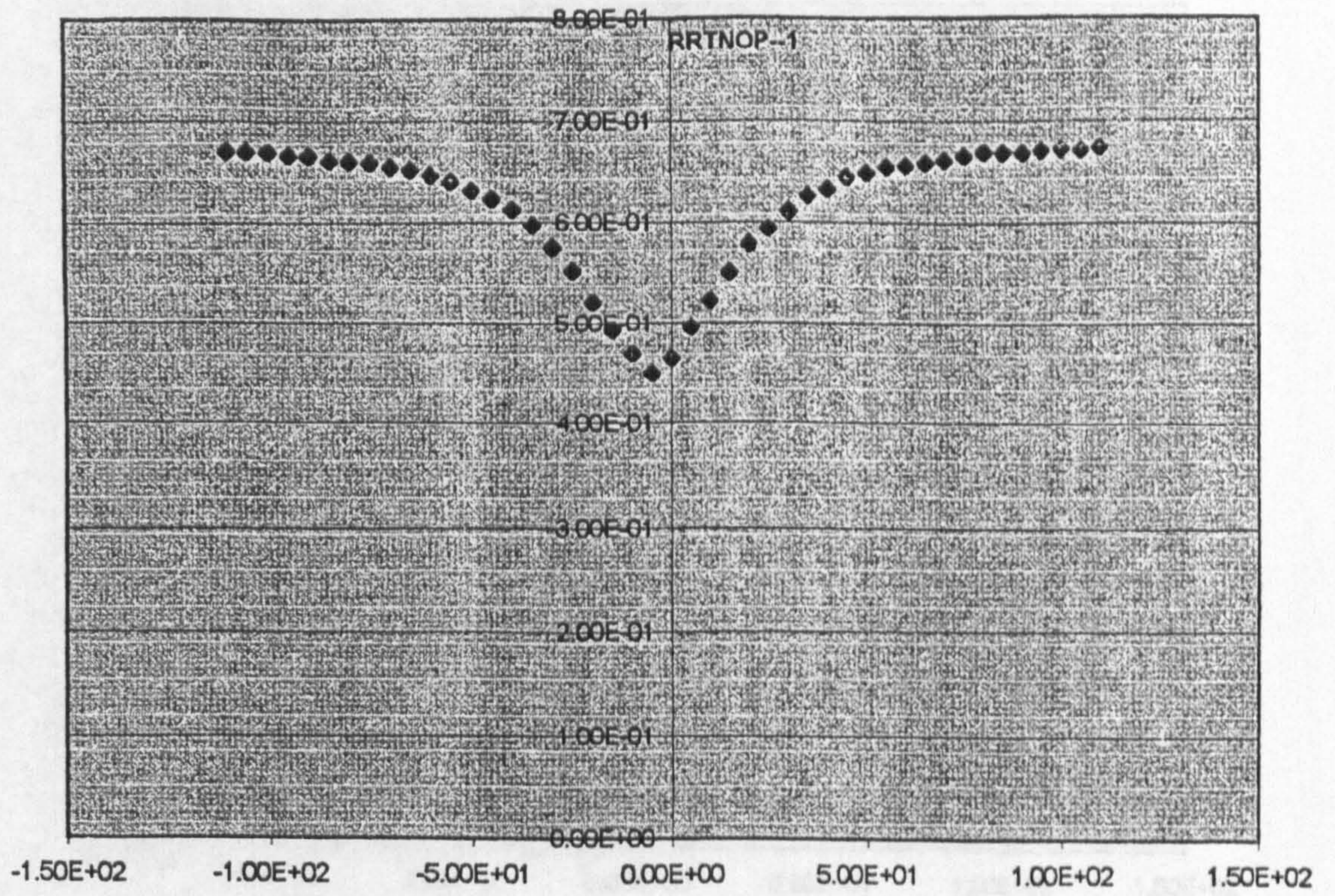


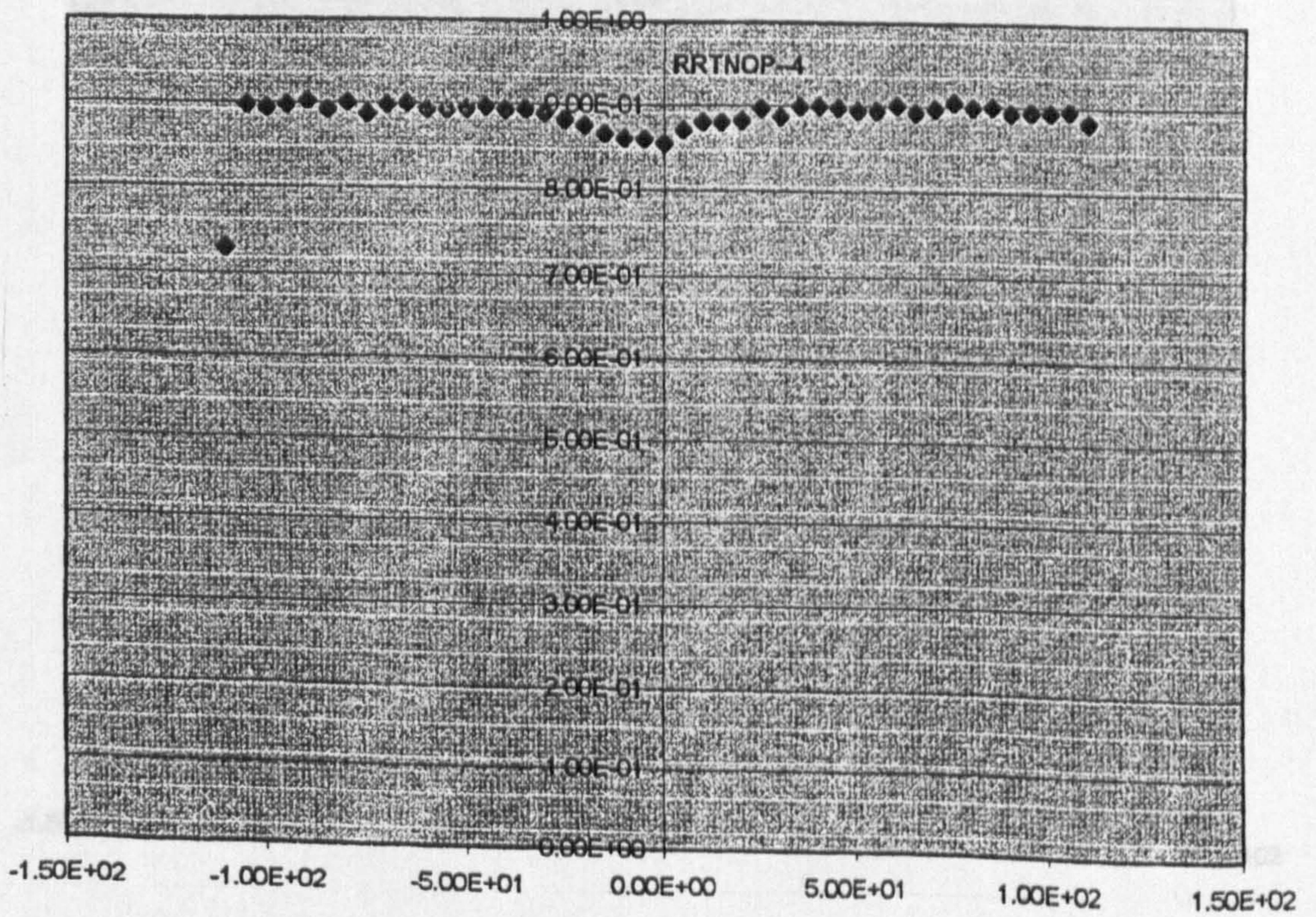
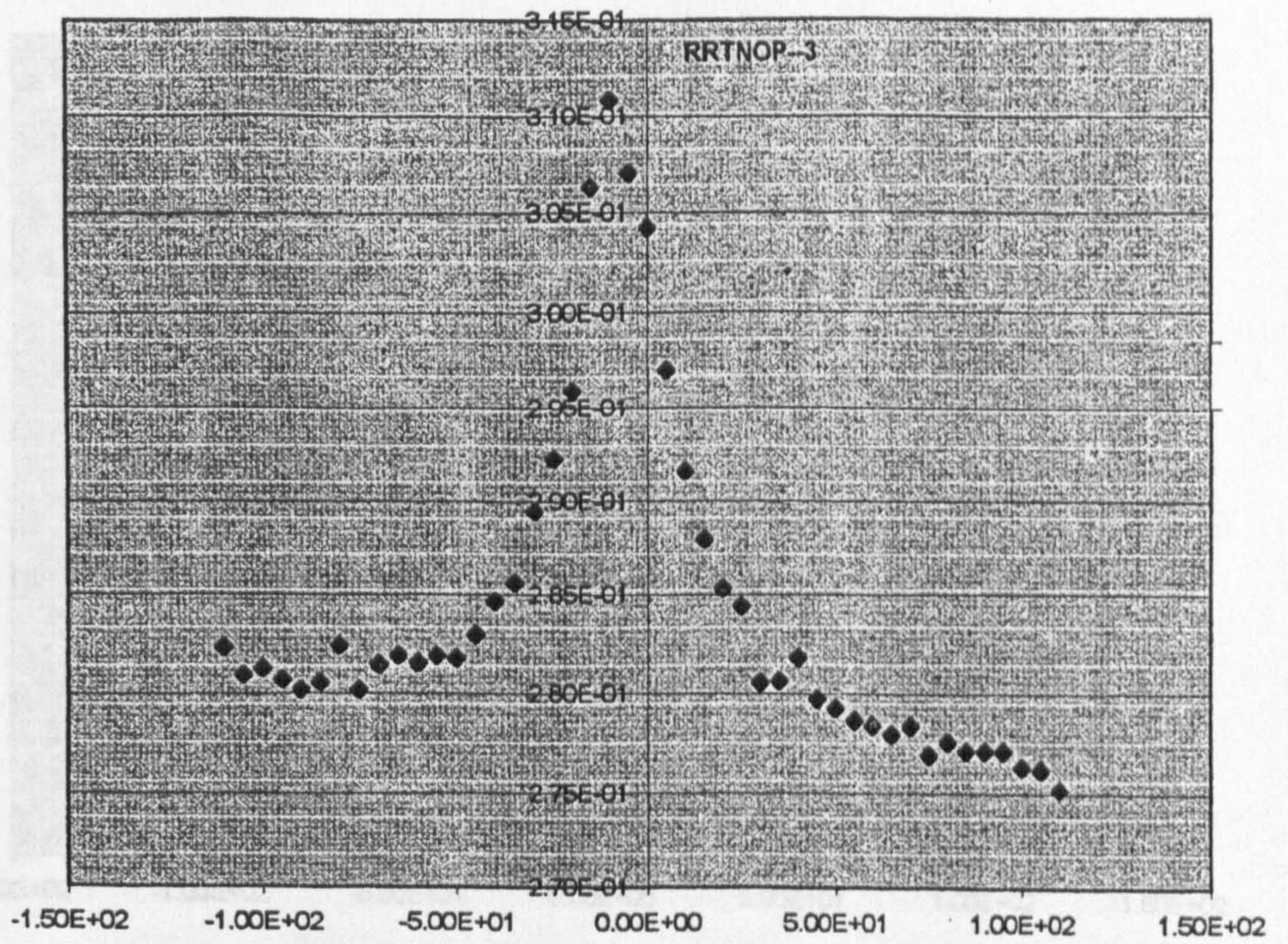


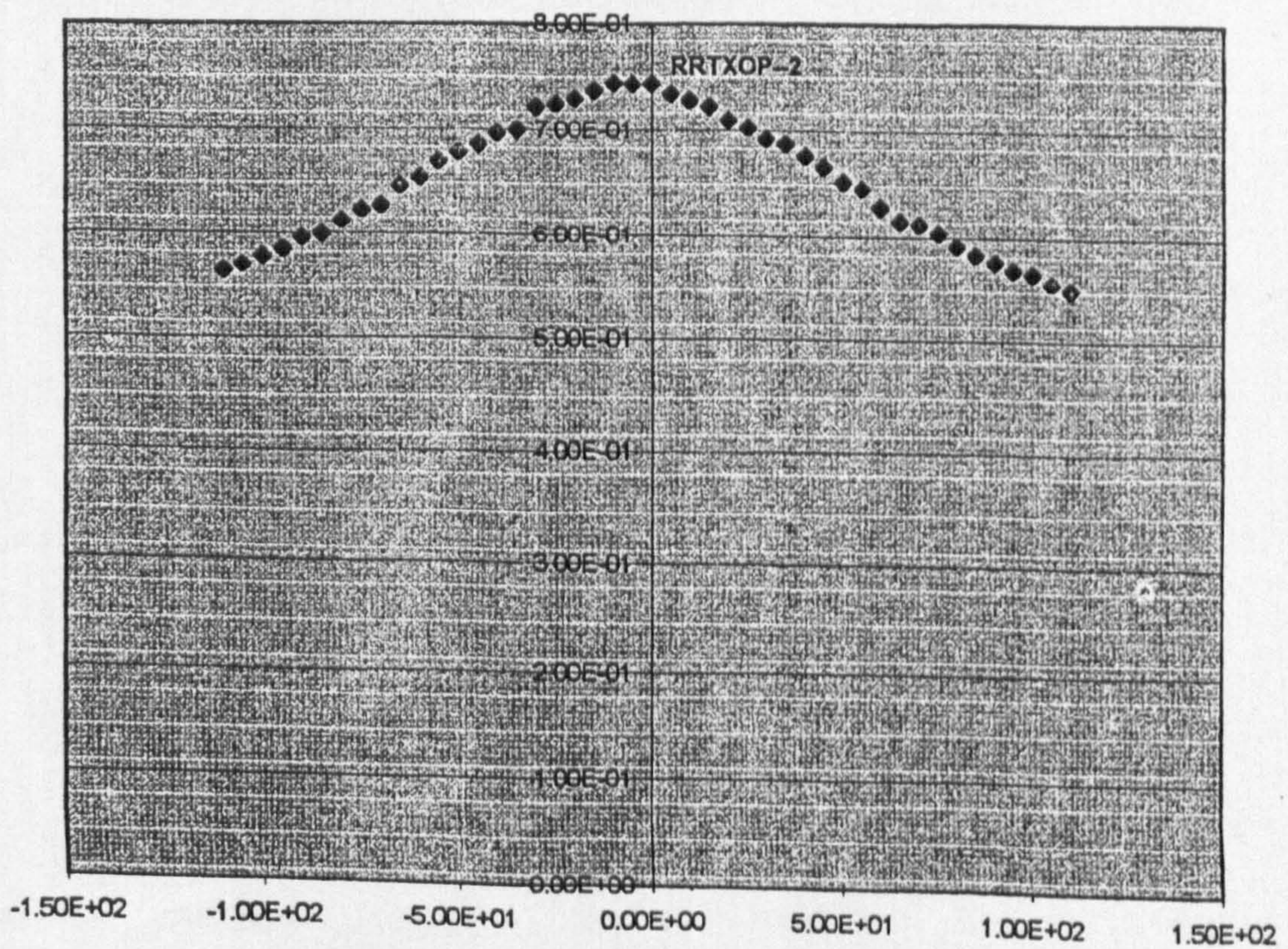
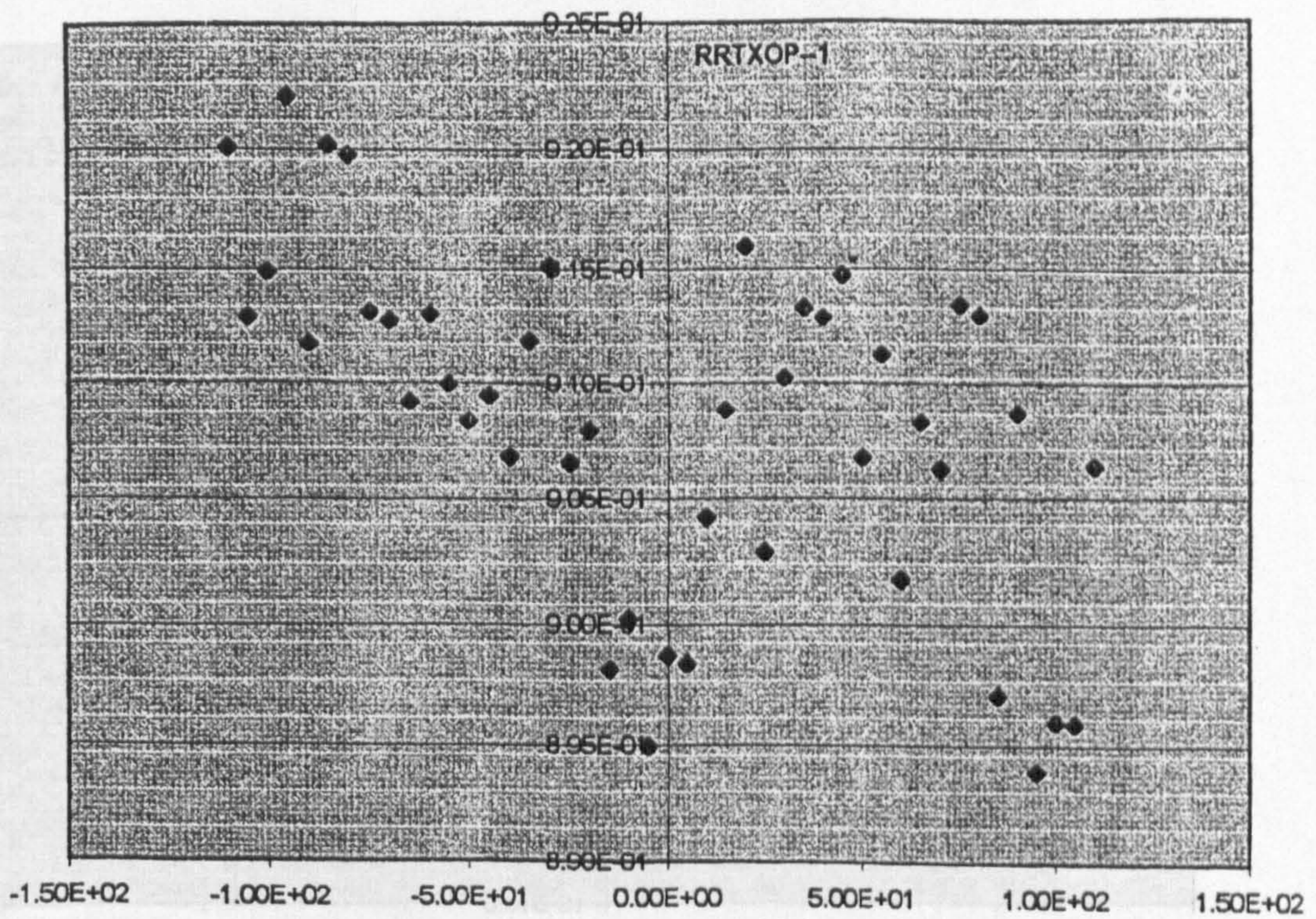


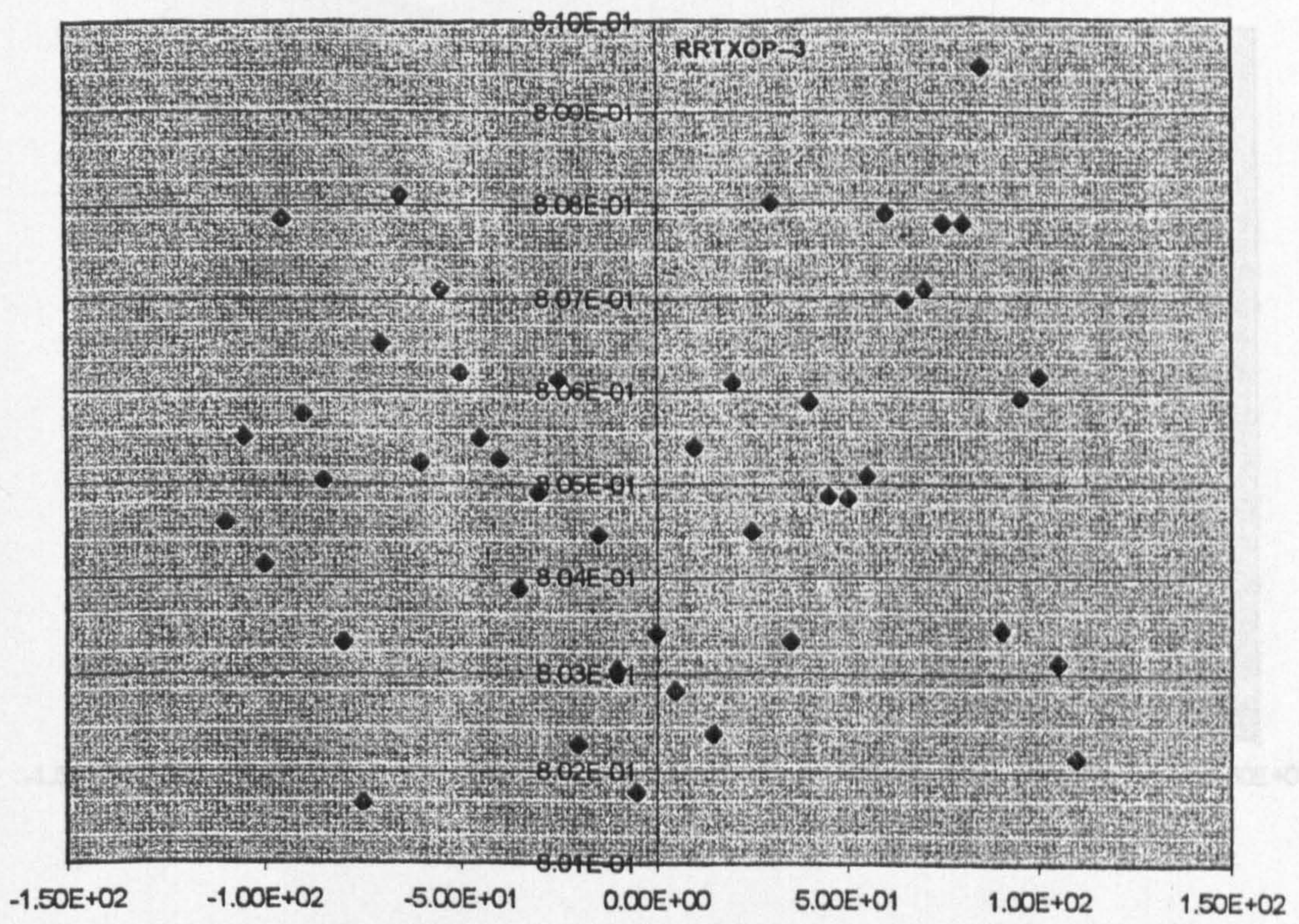


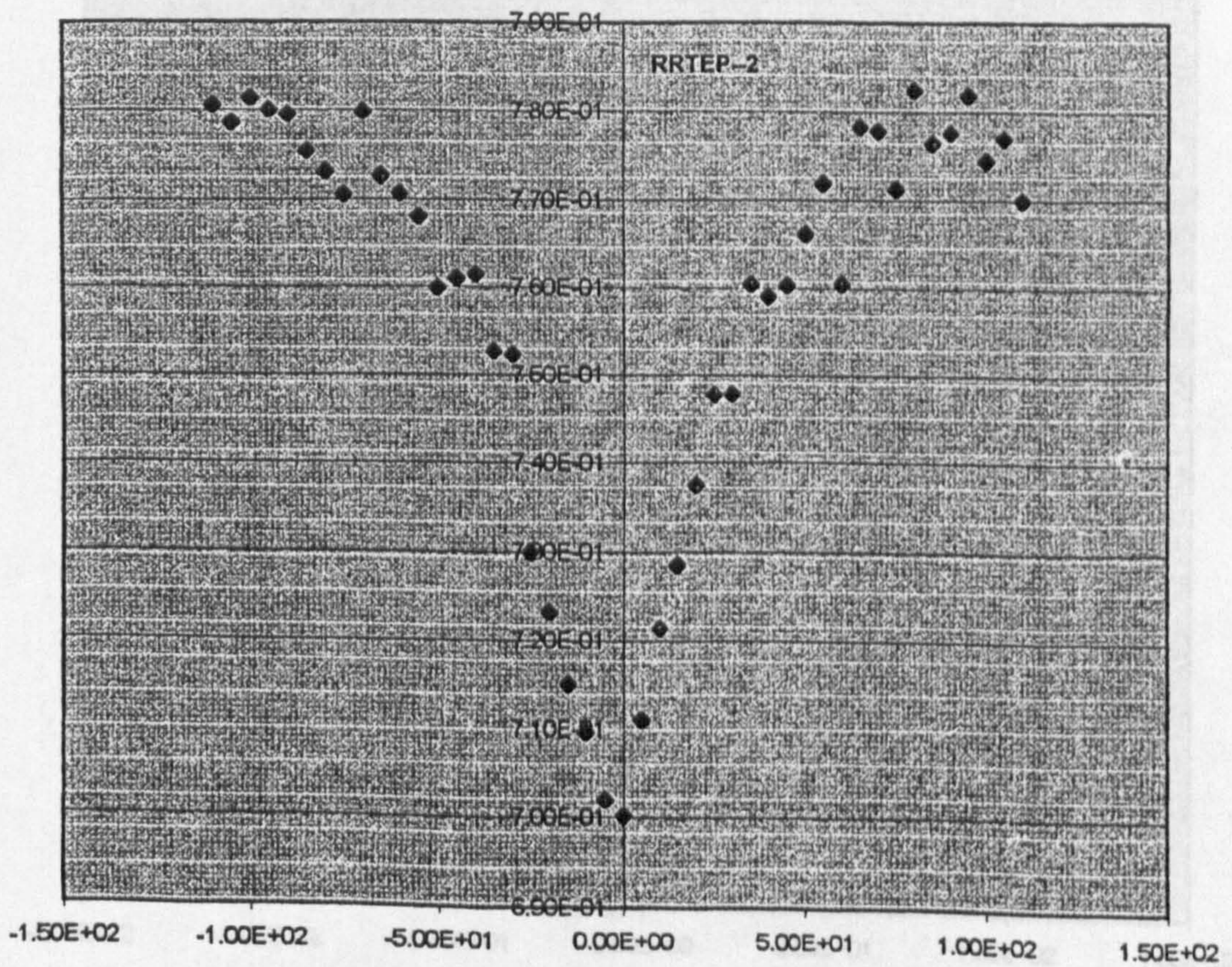
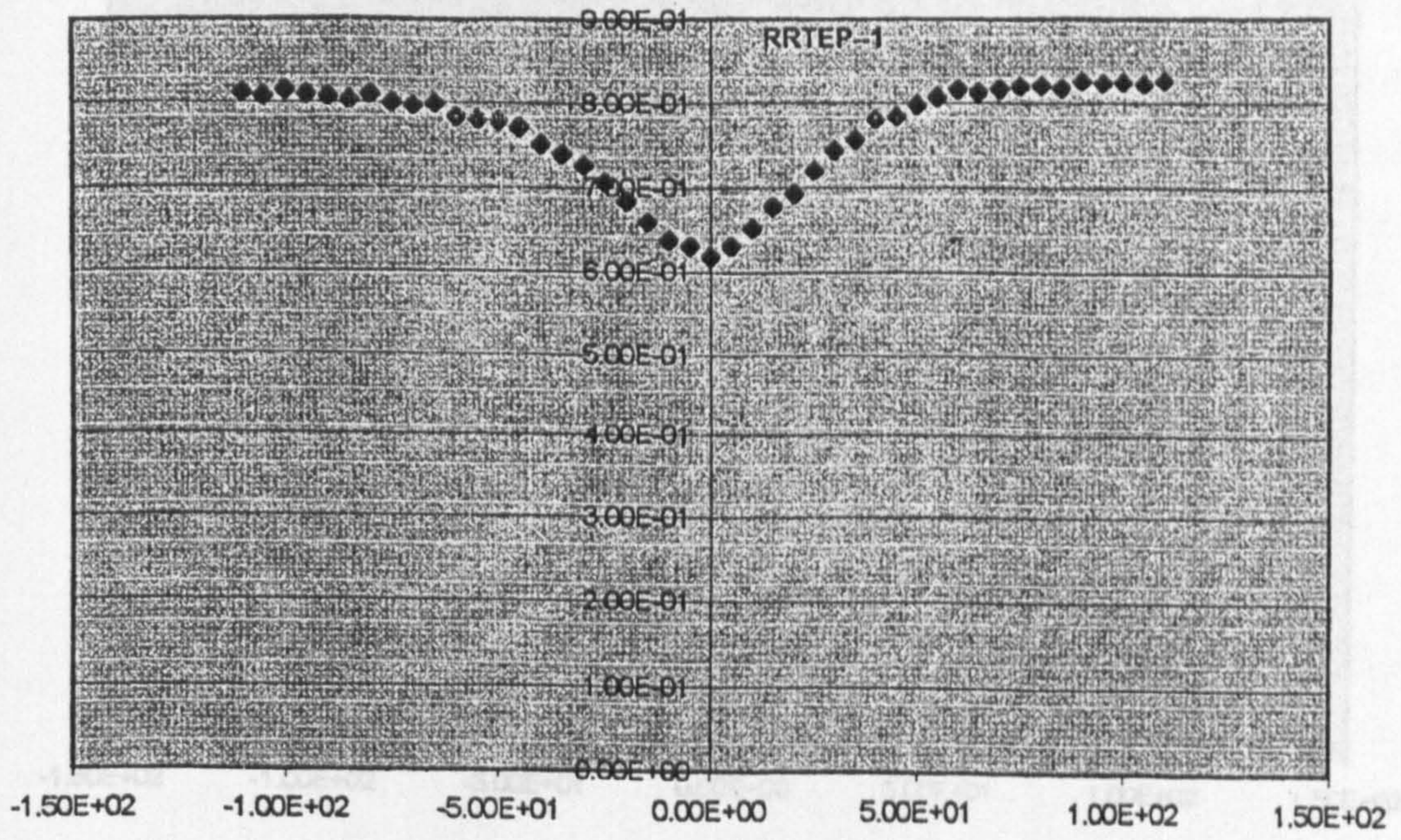




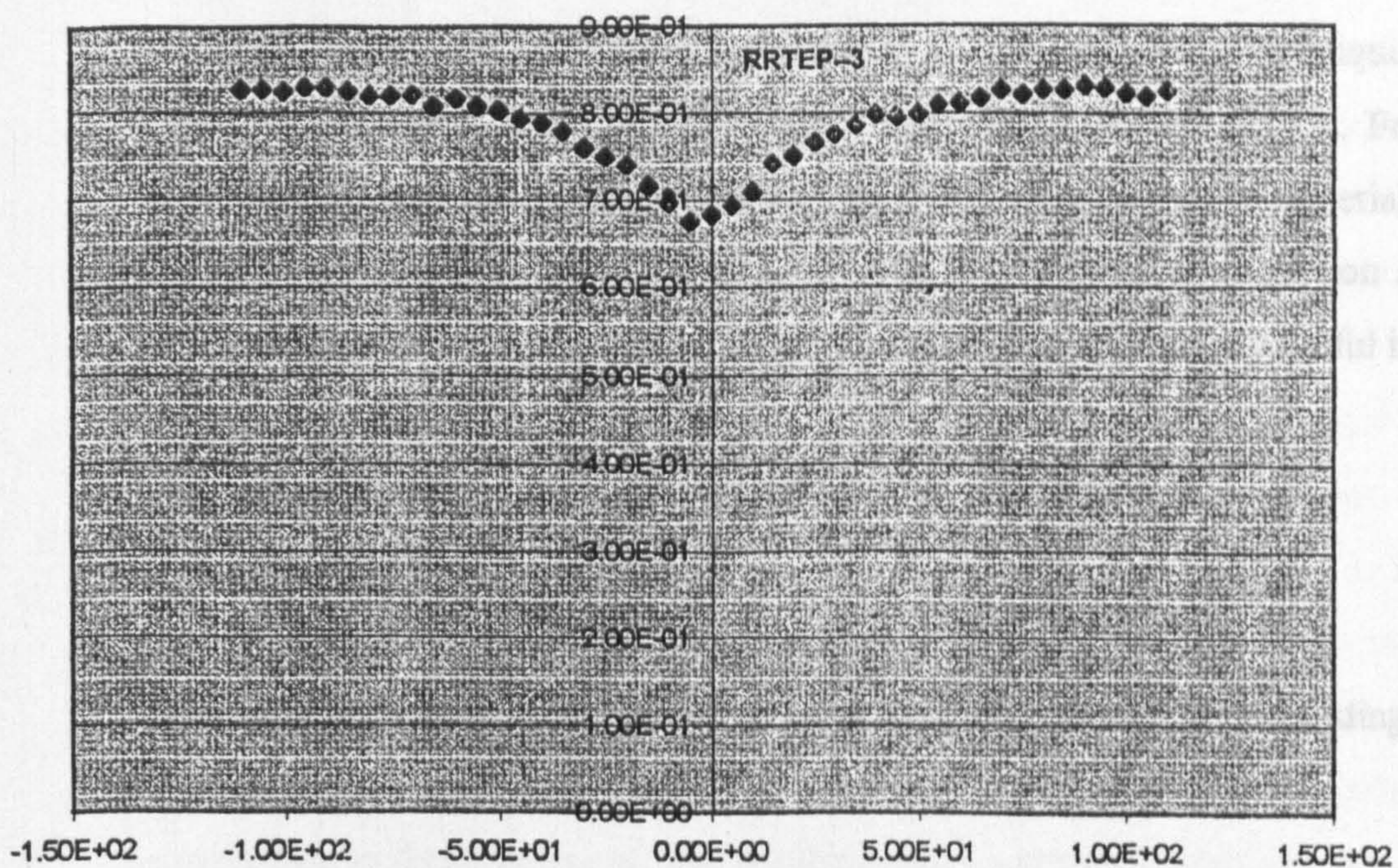




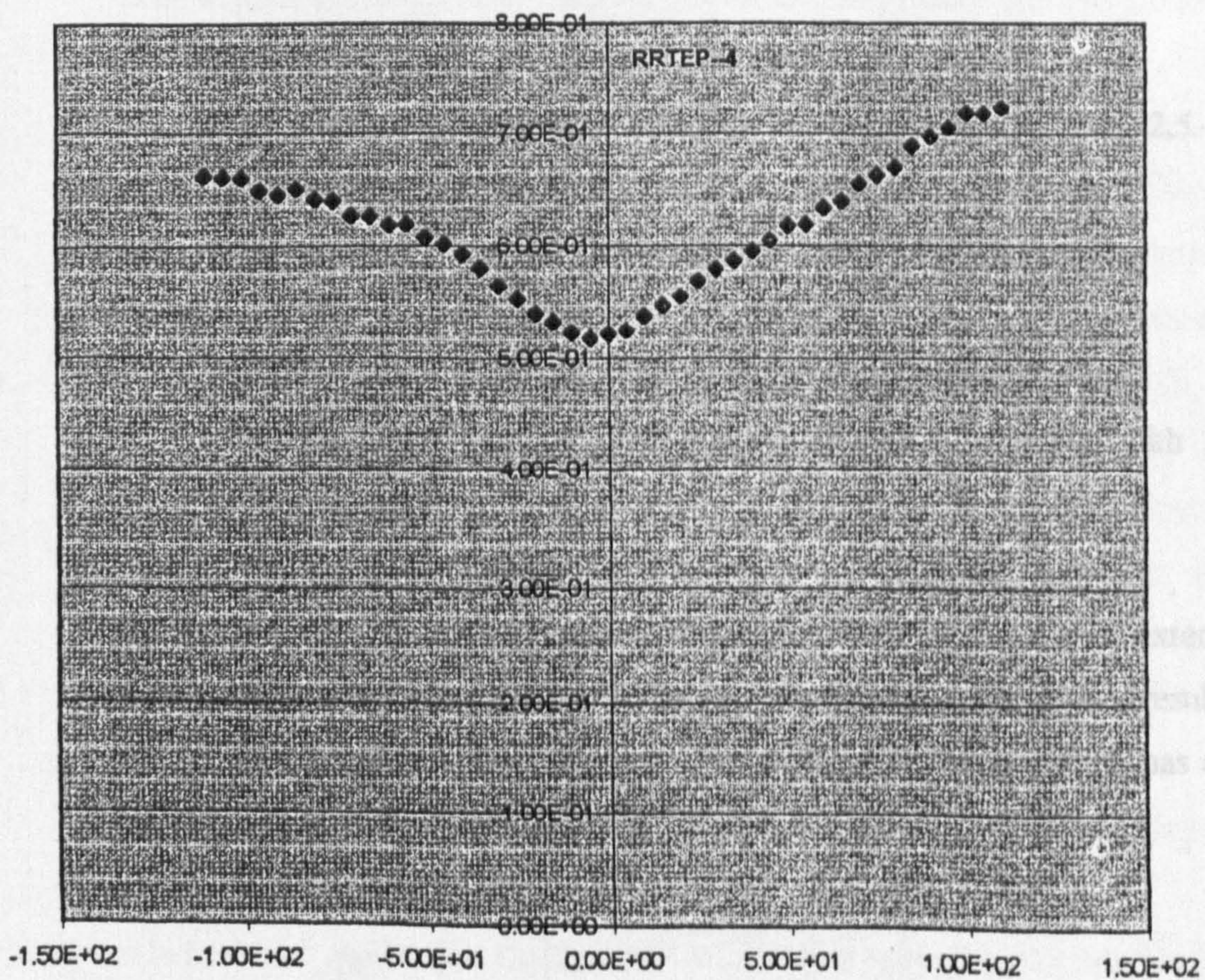








1. *Meso*-pyridyl porphyrins. The parent molecule is the 5,10,15-tris-(3,5-di-*n*-butyl-4-hydroxyphenyl)-20-(4-pyridyl) porphyrin, with the remaining compounds based on a series of alkylations at the 4-pyridyl position.



As already mentioned the Z-scan technique is a useful screening technique to determine whether a material will exhibit reverse saturable absorption. From the data and graphical representations, the RSA potential of a material is obtained by calculating the difference between the % linear transmission and the nonlinear transmission. A material is considered to be potentially useful if:

1. the percentage linear transmission is relatively high, and
2. the difference  $\Delta T$  is large.

The compounds of interest can be grouped into three categories according to their structure:

1. Monopyridyl porphyrins . The parent molecule is the 5,10,15-tris-(3,5-di-t-butyl-4-hydroxyphenyl)-20-(4-pyridyl) porphyrin, with the remaining compounds based on a series of alkylations at the 4-pyridyl position.
2. Oxidised porphyrin. The parent molecule is the 5,15-bis-(3,5-di-t-butyl-4-hydroxyphenyl)-bis-10,20-(3,5-di-t-butyl-4-oxacyclohexa-2,5-dienylene) porphyrin, with the remaining compounds formed as a result of the alkylation of the porphyrins central nitrogen groups.
3. Tetraethynyl porphyrins. A series of porphyrins, symmetrical and unsymmetrical, in which the four meso positions are substituted with ethynyl groups.

Close inspection of Table 5.1 indicates that all the compounds to some extent, exhibit reverse saturable absorption. For an individual compound the results can vary quite considerably for a given wavelength, and each porphyrin has an optimum wavelength at which its RSA potential is greatest.

For the monopyridyl porphyrins, the best results are obtained for the parent molecule. The effects of alkylating the pyridyl position with electron withdrawing groups has led to a less active RSA material. The mentioned parent porphyrin exhibits both characteristics required for RSA materials. At the optimum wavelength of 450nm, this compound exhibits a relatively high linear transmission which drops sharply as it is brought to focus, giving a  $\Delta T$  value of the order of 50%. The relatively high values encountered for this compound indicate that it shows promise as a RSA material. Graphs 5.1-5.12 are a good representation of the trend expected for RSA to be observed. A high linear transmission is observed far from the focus, which decreases to a minimum at the focus, which then increases to a maximum again as the sample is moved away from the focus. The resulting graphs are somewhat symmetrical in shape with the depth of the valley the all important parameter.

Alkylation at the pyridyl position produces compounds that appear to be less promising as RSA materials. The linear transmissions for these materials are in the same region as the parent molecule but the nonlinear transmissions are also high, producing lower  $\Delta T$  values.

The alkylated oxidised porphyrins give results indicating that the use of these materials as RSA is potentially limited. At a wavelength of 640nm the materials all exhibit a large linear transmission value of 90, but again the nonlinear transmissions are also high. The graphical representations for this group of compounds confirm that these materials are not good RSA materials since the scatter graphs do not follow the already mentioned trend. In fact, they appear to observe the opposite trend whereby on bringing the sample to focus, the nonlinear transmission values increase.

Introduction of the ethynyl moiety at the porphyrin's meso-position, should enhance the RSA properties of a material. The values reported for the ethynyl substituted porphyrins indicates that this is the case. The values of  $\Delta T$  associated with the ethynyl compounds are greater in value than the previously

mentioned compounds (with monopyridyl the exception). The limiting factor in how much potential these compounds will exhibit will depend on the degree of linear transmission they possess. The  $\Delta T$  values are quite large ranging from 21-60%, but as already mentioned, a material requires a combination of a large linear transmission as well. The best results exhibited for the ethynyl porphyrins are encountered in the unsymmetrical 2-bromo-5,10,15,20-meso-(4-dodecyloxyphenylethynyl)porphyrin. On introduction of the bromine group to the 2-position of the symmetrical porphyrin, the  $\Delta T$  values increase almost threefold. For the symmetrical porphyrin at a wavelength of 530nm, a large linear transmission is encountered, but a relatively large nonlinear transmission is also encountered, resulting in a moderate  $\Delta T$  value. Introduction of the bromine group has the effect of lowering the linear transmission by 20% but at the same time lowering the non-linear transmission by almost 55%, thus producing a very large  $\Delta T$  value.

The introduction of the ethynyl groups does have an enhanced effect on the RSA properties of the above mentioned compounds. Also, as demonstrated in table 5.1. the greater the unsymmetrical nature of the porphyrin, the better the results appear. The introduction of the bromine group to the symmetrical porphyrin does result in a threefold increase in the RSA potential.

For a more detailed, accurate analysis of the RSA potential of the above materials, more information regarding excited state lifetimes is required. As mentioned, the work performed at this stage is purely as a screening device, but the results for some of the above mentioned compounds appear to be promising and further work is required to gain a more detailed outlook.

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## 6 CONCLUSION

The RSA characteristics of several porphyrin materials have been measured by means of a Z-scan technique. However, this has been performed primarily in an attempt to observe and not fully investigate. In order to carry out further investigation, more information is required, including such information as excited state lifetimes. Despite this, the transmission measurements are a useful screening device to indicate whether or not the porphyrin macrocycles show potential as RSA materials.

There appears to be a limiting threshold above which porphyrins will be candidates for further investigation as RSA materials. It is difficult to make firm structure-property relationships, due to the number of porphyrins that were utilised. From our observations, it can be said that RSA was observed to some extent in all the porphyrins tested. The oxidised porphyrins, on the other hand, showed little or no RSA properties and this could be an effect of losing the porphyrin aromaticity on oxidising the porphyrin.

The electronic absorption spectra of the oxidised porphyrins are characterised by the loss of the intense porphyrinic B band and replaced by a broad, relatively intense absorption around 500- 510 nm. The <sup>1</sup>H nmr of the oxidised porphyrin indicates the loss of aromaticity by the appearance of the N-H protons at low field. Alkylation of the oxidised porphyrin results in macrocycles that are structurally the same and therefore, also lacking the porphyrin's aromaticity. Even though the oxidised porphyrins possess an extended conjugated system the lack of porphyrin aromaticity appears to reduce the potential this group of compounds possess as RSA materials.

Initial results indicate that the 5,10,15 tris-(3,5-di-t-butyl-4-hydroxyphenyl)-20-(4-pyridyl) porphyrin has the potential to be a useful RSA material.

Further investigation is needed to confirm the full potential of the compound, but as demonstrated from the results, the initial signs look favourable.

The potential this porphyrin exhibits is excellent because not only does it produce good results, it is also a porphyrin that is very readily synthesised by the mixed condensation reaction of the appropriate aldehydes with pyrrole.

The alkylation of the 4-pyridyl position with electron withdrawing groups to form the quaternised nitrogen leads to compounds where the RSA potential is reduced. Peripheral extensions are seen as a versatile approach to tuning the porphyrin absorption spectrum and hence, the RSA properties. The quaternisation of the pyridyl nitrogen gives an extended macrocycle, but the conjugation is lost through the benzylic bond and this could be the important factor why enhanced RSA properties are not observed.

We have successfully shown that a new class of porphyrin macrocycle can be synthesised, by the introduction of four ethynyl moieties at the peripheral meso-positions. This has led to considerable changes in the electronic absorption spectra, with large red shifts encountered for the porphyrin B and Q bands. Also, there is a marked increase in the main Q band absorption relative to that of the B band. This illustrates that the ethynyl groups mediate communication between the porphyrin and the aryl pi-systems more efficiently than when the aryl group is connected directly to the porphyrin macrocycle. Due to this electronic coupling of the macrocycle, ethynyl group and aryl substituents, the potential for these molecules to have enhanced RSA properties is experienced.

One noticeable feature observed from the electronic absorption spectra of the mentioned ethynyl porphyrins, is that the biggest red shifts are encountered when the porphyrin's substitution is unsymmetrical.

This characteristic difference is noticeable in the RSA values for the ethynyl porphyrins, with the unsymmetrical porphyrins having a more enhanced effect than the symmetric ethynyl porphyrins.

To gain a better understanding of the relationship between structure -property and the difference caused by symmetry, a more detailed study needs to be undertaken.

We can conclude from our initial studies that reverse saturable absorption is experienced in both the symmetric and unsymmetrical porphyrins. It is evident that the effect is enhanced when the porphyrin is unsymmetrical.

Finally, we can conclude that the introduction of the ethynyl moiety directly onto the porphyrin ring enhances RSA. The extended delocalisation pathway that is experienced when the ethynyl group is introduced enables more electronic overlap and hence more communication between the macrocycle and the aryl substituents. This in turn leads to an enhanced effect, which needs to be fully investigated.



## 7 Experimental

UV/visible spectra were recorded on a Cecil CF 5500 double beam UV spectrophotometer and a HP8453 diode array spectrophotometer, using spectroscopic grade chloroform and dichloromethane as solvents.  $^1\text{H}$  NMR spectra were recorded on a Jeol JNM FX200 instrument in  $\text{CDCl}_3$  using TMS (tetramethylsilane) as an internal reference. Mass spectra were recorded on a AEI MS902 spectrometer or at the EPSRC facility (Department of Chemistry, University of Wales, Swansea) for fast atom bombardment (FAB) and accurate mass measurements (reference standard, polyethylene glycol). Infra-red spectra were recorded as KBr discs using a Perkin-Elmer 1420 Ratio Recording Infra-Red spectrophotometer.

TLC was performed on Aldrich aluminium backed silica-gel 60  $\text{F}_{254}$  plates and neutral alumina 60  $\text{F}_{254}$  type E plates. Porphyrins were separated via column chromatography on neutral alumina (Brockmann III, 150 mesh). Solvents and reagents were supplied by Aldrich and used as supplied.

Synthesis of 5,10,15-tris-(3,5-di-t-butyl-4-hydroxyphenyl)-20-(4-pyridyl) porphyrin 24 - Pyrrole (6.7 gm, 0.1 mole) and pyridine-4-carboxaldehyde (5.35 gm, 0.05 mole) were added to refluxing propionic acid (500 mls) containing 3,5-di-t-butyl-4-hydroxybenzaldehyde (11.6 gm, 0.05 mole) and refluxed for 3 hours. The reaction mixture was concentrated to one fifth of its original volume by distillation, and the remaining propionic acid taken off under reduced pressure. After cooling, the solid residue was triturated with acetone (500 mls) several times and filtered to give a mixture of porphyrins as a purple amorphous powder. The mixture was purified by column chromatography on alumina eluting with dichloromethane (DCM), then after concentrating the eluant, rechromatographed on alumina, eluting with 60 : 40 DCM : n-hexane. The first fraction eluted off the column was concentrated and precipitated with n-hexane to yield the well established symmetrical 5,10,15,20-tetrakis-(3,5-di-t-

butyl-4-hydroxyphenyl) porphyrin **23**<sup>(1)</sup> (600mg, 2%). The second fraction to be eluted from the column was concentrated and recrystallised with n-hexane to yield the unsymmetrical 5,10,15-tris-(3,5-di-t-butyl-4-hydroxyphenyl)-20-(4-pyridyl) porphyrin **24**<sup>(2)</sup> (1g, 2.5%) as purple microcrystals.

$\lambda_{\max}$  nm ( $\epsilon$  mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>) 424 (420000), 520 (14000), 559 (4000) 651 (5500).

FAB-MS (3-NOBA, CHCl<sub>3</sub>): found  $m/z = 1000$ , [M+H]<sup>+</sup> requires  $m/z = 1000$ .

$\delta_{\text{H}}$  (ppm): 9.04, 9.01, 8.20, 8.17 (quartet, 4H, AB spin-system for pyridyl-H,  $J_{\text{AB}} = 5.86\text{Hz}$ ); 8.94 (s,4H, pyrrole- $\beta$ -H remote from pyridyl group); 8.97, 8.95, 8.79, 8.76 (quartet, 4H, pyrrole- $\beta$ -H, adjacent to pyridyl group,  $J_{\text{AB}} = 5.17\text{Hz}$ ); 8.03 (s,6H, DtBHP ortho-H); 5.55 (s,3H, phenolic-OH) 1.63 (s,54H,t-butyl-H); - 2.69 (broad singlet, 2H, N-H).

#### **N-Alkylations of porphyrin 24**

Alkylation of Porphyrin 24 with benzyl bromide - Porphyrin **24** (250mg,  $2.5 \times 10^{-4}$  mol) was refluxed with neat benzyl bromide (110mg,  $5.8 \times 10^{-4}$  mol) for three hours. The mixture was subjected to column chromatography, firstly eluting with chloroform, then increasing the polarity by adding methanol. The first band eluted from the column was the unreacted benzyl bromide and on increasing the polarity the 5,10,15-tris (3,5-di-t-butyl-4-hydroxyphenyl)-20-(4-[benzyl] pyridiniumyl) porphyrin bromide **25**<sup>(2)</sup> (170 mg, 60%) was eluted as a purple powder.

$\lambda_{\max}$  nm ( $\epsilon$  mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>) 431 (128000), 527 (5000), 578 (10000), 662 (4500). FABS-MS (3-NOBA, CHCl<sub>3</sub>) found  $m/z = 1091$ ; [M- Br]<sup>+</sup> requires  $m/z = 1091$ .

<sup>1</sup>H NMR  $\delta$  (ppm): 9.766, 9.733, 8.772, 8.739 (quartet, 4H, AB spin system from 4-pyridinium - H,  $J_{\text{AB}} = 6.6\text{Hz}$ ); 8.94 (s,4H, pyrrole- $\beta$ -H remote from 4-pyridinium group); 9.014, 8.992, 8.794, 8.772 (quartet, 4H, pyrrole- $\beta$ -H, adjacent to 4-pyridinium group,  $J_{\text{AB}} = 4.4\text{Hz}$ ); 8.01 (s,6H, DtBHP ortho-H), 7.90, 7.87, 7.53, 7.50 (multiplet, 5H, benzylic-H); 6.62 (s,2H, benzylic-CH<sub>2</sub>);

5.58 (s,3H, phenolic-OH); 1.63 (s,54H, t-butyl-H); -2.55 (s,2H, porphyrin N-H).

Alkylation of porphyrin 24 with 4-nitrobenzylbromide - Porphyrin 24 (100mg,  $1 \times 10^{-4}$  mol) was refluxed with excess 4-nitrobenzylbromide (1.1 gm,  $5 \times 10^{-3}$  mol) in DMF (50 ml) for three hours. After the removal of solvent, the resulting dark solid was dissolved in acetone, filtered, evaporated to dryness and the residue taken into a small amount of chloroform. This was columned on alumina, eluting with chloroform/methanol 95 : 5 to yield meso-5,10,15-tris-(3,5-di-t-butyl-4-hydroxyphenyl)-20-(4-[4-nitrobenzyl]pyridiniumyl)porphyrin bromide 26<sup>(2)</sup> as a purple amorphous powder (120 mgs 90%). ( found : C, 71.53; H, 7.26; N, 6.74,  $C_{74}H_{83}N_6O_5$  Br.  $1.5H_2O$  requires C, 71.48; H, 6.97; N, 6.76%).  $\lambda_{max}$  nm ( $\epsilon$  mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>) 425 (130000), 512 (5500), 595 (10000), 665 (4500). FAB-MS (3-NOBA,  $CHCl_3$ ): found  $m/z = 1136$ ,  $[M-Br]^+$  requires  $m/z = 1136$ .  $\delta_H$  (ppm) 9.86, 9.83, 8.82, 8.79 (quartet, 4H, AB spin system from 4-pyridinium-H,  $J_{AB} = 5.86$  Hz); 8.94 (s, 4H, pyrrole- $\beta$ -H remote from pyridinium group); 9.04, 9.01, 8.77, 8.75 (quartet, 4H, pyrrole- $\beta$ -H adjacent to 4-pyridinium group,  $J_{AB} = 5.13$ Hz), 8.08, 7.97, 6.83, 6.72 (quartet, 4-H, 4-nitrobenzyl-H,  $J_{AB} = 8.4$  Hz), 8.02 (s,6H, DtBHP ortho-H), 5.58 (s,3H, phenolic-OH); 4.64 (broad singlet, 2H, 4-nitrobenzylic-  $CH_2$ ); 1.3 (complex singlet, 54H, t-butyl-H); -2.53 (broad singlet, 2H, porphyrin N-H).

Alkylation of porphyrin 24 with  $\alpha,\alpha'$ -di-bromo-*p*-xylene - Porphyrin 24 (250 mg,  $2.5 \times 10^{-4}$  mol) was refluxed in toluene (50 ml) and  $\alpha,\alpha'$ -di-bromo-*p*-xylene (1.32 g,  $5 \times 10^{-3}$  mol) was added and refluxed for a further 3 hours. After removal of solvent the solid residue was subjected to column chromatography on alumina eluting with 95 : 5 chloroform/methanol. The first band eluted off the column was the unreacted porphyrin 24 (25 mg, 10%) as a purple powder. The second band eluted off the column was concentrated to give a purple powder (160 mg, 51%) which was characterized as the monoalkylated

unsymmetrical 5,10,15-tris-(3,5-di-t-butyl-4-hydroxyphenyl)-20-(4-[4-bromomethylbenzyl]pyridiniumyl) porphyrin bromide **27**. ( found : C, 69.89; H, 6.58; N, 5.26 C<sub>75</sub>H<sub>85</sub>N<sub>5</sub>O<sub>3</sub>Br<sub>2</sub>. 1.5 H<sub>2</sub>O requires C, 69.76; H, 6.87; N, 5.42%).  $\lambda_{\max}$  nm ( $\epsilon$  mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>) 430 (130000), 527 (4000), 578 (11000), 662 (5000). FAB-MS (3-NOBA, CHCl<sub>3</sub>) found  $m/z$  - 1185, 1104, 1000, [M-Br]<sup>+</sup> requires  $m/z$  = 1185; [M-2Br]<sup>+</sup> requires  $m/z$  = 1104. <sup>1</sup>H nmr  $\delta$ (ppm) 9.832, 9.799, 8.761, 8.728 (quartet, 4H, AB spin system from 4-pyridinium - H, J<sub>AB</sub> = 6.6 Hz); 8.94 (s, 4H, pyrrole  $\beta$ -H remote from pyridinium group); 9.018, 8.996, 8.783, 8.761 (quartet, 4H, pyrrole  $\beta$ -H adjacent to 4 pyridinium group, J<sub>AB</sub>= 4.4 Hz); 8.02 (s, 6H, DtBHP ortho-H); 7.913, 7.872, 7.476, 7.435 (quartet, 4H, aromatic -H, J<sub>AB</sub> = 8.2Hz); 6.61 (s,2H,4-bromomethylbenzyl CH<sub>2</sub>); 5.59 (s,3H, phenolic-OH); 4.35 (s,2H, CH<sub>2</sub>Br); 1.63 (s,54H, t-butyl-H); -2.56 (s,2H, porphyrin N-H).

The third band eluted from the column was concentrated to yield the dimer as a dark purple powder **28** ( 180mg, 14%).

$\lambda_{\max}$  nm ( $\epsilon$  mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>) 430 (125000), 528 (4000), 575 (11000), 660 (4500), FABS-MS (3NOBA; CHCl<sub>3</sub>) found  $m/z$  = 1000, 2106, 2187, [M-Br]<sup>+</sup> requires  $m/z$  = 2187; [M-2Br]<sup>+</sup> requires  $m/z$  = 2106, [(M-2Br) - [benzyl] - porphyrin) requires  $m/z$  = 1000. <sup>1</sup>Hnmr  $\delta$  (ppm) 9.752, 9.719, 8.783, 8.750 (quartet, 8H, AB spin system from 4-pyridinium-H, J<sub>AB</sub> = 6.6Hz); 9.021, 8.999, 8.794, 8.772 (quartet, 8H, pyrrole  $\beta$ -H remote from pyridinium group, J<sub>ab</sub> = 4.4Hz); 8.01 (s, 12H, DtBHP ortho-H); 7.905, 7.872, 7.568, 7.535 (quartet, 4H, aromatic -H, J<sub>AB</sub> = 6.6Hz), 6.61 (s, 4H, xylene -CH<sub>2</sub>), 5.59 (s,6H, phenolic -OH), 1.63 (s, 108H, t-butyl-H), -2.56 (S,4H, porphyrin N-H).

Alkylation of porphyrin **24** with  $\alpha,\alpha'$ -di-bromo-*o*-xylene - Porphyrin **24** (350 mg, 3.5x10<sup>-4</sup> mol) was refluxed for 3 hours with  $\alpha,\alpha'$ -di-bromo-*o*-xylene (46mg, 1.75x10<sup>-4</sup> mol) in dry toluene (20mls). The solvent was removed under vacuum and the residue was subjected to column chromatography on silica eluting with a 50:50 mixture chloroform/acetonitrile. The first fraction eluted was the

unreacted 5,10,15-tris-(3,5-di-*t*-butyl-4-hydroxyphenyl)-20-(4-pyridyl) porphyrin. The second band to be eluted was evaporated to dryness to yield a purple solid **29** (0.12g, 27%) which contained some impurities. <sup>1</sup>H nmr studies indicated the isolation of the monoalkylated species but several attempts to re-column and recrystallise proved unsuccessful. The third band eluted from the column was evaporated to dryness to yield the ortho dimer (317mg, 40%) as a purple solid **30**. ( found C, 71.58; H, 7.01; N, 5.69; C<sub>142</sub> H<sub>162</sub> N<sub>10</sub> O<sub>6</sub> Br<sub>2</sub>.CHCl<sub>3</sub> requires C, 72.04; H, 6.89; N, 5.88 %). λ<sub>max</sub> nm (ε mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>) 428 (126000), 528 (5000), 579 (10000), 662 (5500). FABS-MS (3-NOBA, CHCl<sub>3</sub>) found <sup>m/z</sup> = 2185, 2104, 1104, 1000; [(M-Br)<sup>+</sup> requires <sup>m/z</sup> = 2185; [M-2Br)<sup>+</sup> requires <sup>m/z</sup> = 2104 (M-2Br)-(porphyrin) requires <sup>m/z</sup> = 1104, [(M-2Br)-(benzyl)-(porphyrin)] requires <sup>m/z</sup> = 1000. <sup>1</sup>Hnmr δ(ppm) 9.723, 9.706, 9.142, 9.125 (quartet, 8H, AB spin system from 4-pyridinium-H, J<sub>AB</sub> = 6.12 Hz), 9.081, 9.068, 8.979, 8.966 (quartet, 8H, pyrrole β-H, adjacent to 4-pyridinium group, J<sub>AB</sub> = 4.68 Hz), 8.89 (s, 8H, pyrrole β-H remote from pyridinium group), 7.96 (s, 8H, DtBHP ortho-H adjacent to 4-pyridinium group), 7.93 (s, 4H, DtBHP ortho-H remote from 4-pyridinium group), 7.85 (broad s, 4H, aromatic H), 7.47 (s, 4H, phenolic-OH adjacent to 4-pyridinium group), 7.46 (s, 2H, phenolic-OH remote from 4-pyridinium group), 6.76 (broad s, 4H, -benzylic- CH<sub>2</sub>) 1.60 (complex s, 108H, *t*-butyl H), -2.59 (s, 4H, porphyrin N-H).

#### **Metallation of compounds 24,25,26and 27, with MnCl<sub>2</sub>-**

##### meso-5,10,15-tris-(3,5-di-*t*-butyl-4-hydroxyphenyl)-20-(4-pyridyl)

porphyrinatomanganese - An excess of MnCl<sub>2</sub>.4H<sub>2</sub>O (1g, 3.75x10<sup>-3</sup>mol) was brought to reflux in DMF (30mls) upon which porphyrin **24** was added (0.1g, 1x10<sup>-4</sup> mol) and the reaction was monitored by UV spectroscopy. After 10 minutes the reaction was stopped, allowed to cool to room temperature and the solvent removed under reduced pressure. The resulting residue was subjected to column chromatography on alumina eluting with 95:5 chloroform/methanol. The first band eluted was the unreacted porphyrin as a minor fraction. The

major band eluted from the column was reduced in volume and recrystallised from chloroform/hexane to yield the meso-5,10,15-tris-(3,5-di-t-butyl-4-hydroxyphenyl)-20-(4-pyridyl) porphyrinato manganese chloride 31 as a green amorphous powder (0.087 mg, 83%). ( found: C, 72.83; H, 6.94; N, 6.24 -  $C_{67}H_{75}N_5O_3MnCl \cdot H_2O$  requires. C, 72.71; H, 7.01; N, 6.33%). FABS-MS (3-NOBA,  $CHCl_3$ ) found  $m/z = 1088, 1053$ ; [M] requires  $m/z = 1088$ , [M-Cl]<sup>+</sup> requires  $m/z = 1053$ .  $\lambda_{max}$  nm ( $mol^{-1} dm^3 cm^{-1}$ ) 482 (130000), 589.5 (13000) 628 (19400).

meso-5,10,15-tris-(3,5-di-t-butyl-4-hydroxyphenyl)-20-(4-{benzyl}pyridiniumyl)porphyrinatomanganese bromide - To an excess of  $MnCl_2 \cdot 4H_2O$  (1g,  $3.75 \times 10^{-3}$  mol) refluxing in DMF (30 ml), porphyrin 25 (0.12g,  $1 \times 10^{-4}$  mol) was added and the reflux continued for 25 minutes. The reaction mixture was cooled and the excess solvent was removed under reduced pressure. The mixture was dissolved in water and the porphyrin was extracted several times with chloroform. The solvent was dried over magnesium sulphate, filtered, reduced in volume and subjected to column chromatography on alumina eluting with 95:5 chloroform: methanol mixture. The major band eluted from the column was reduced in volume and recrystallised from chloroform/hexane to yield the meso-5,10,15-tris-(3,5-di-t-butyl-4-hydroxyphenyl)-20-[{4-benzyl}pyridiniumyl] porphyrinatomanganese bromide 32 as a green amorphous powder (0.085mg, 68%). ( found : C, 71.69; H, 7.17; N, 5.22.  $C_{74}H_{82}N_5O_3 MnBrCl \cdot C_6H_{14}$  requires C, 71.39; H, 7.19; N, 5.20%).  $\lambda_{max}$  nm ( $\epsilon mol^{-1} dm^3 cm^{-1}$ ) 485 (87000) , 592 (9400), 633 (13600) . FABS-MS (3-NOBA,  $CHCl_3$ ). Found:  $m/z = 1179, 1144, 1053$ ; [M-Br]<sup>+</sup> = 1179, [(M-(Br)-(Cl))] requires  $m/z = 1144$ ; [(M-(Br)<sup>+</sup> - (Cl) - (benzyl))] requires  $m/z = 1053$ .

meso-5,10,15-tris-(3,5-di-t-butyl-4-hydroxyphenyl)-20-(4-{4-nitrobenzyl}pyridiniumyl) porphyrinatomanganese bromide - To an excess of  $MnCl_2 \cdot 4H_2O$  (1g,  $3.75 \times 10^{-3}$  mol) refluxing in DMF (30ml), porphyrin 26 was added (0.12g,  $1 \times 10^{-4}$  mol) and the mixture refluxed for 10 minutes. The reaction mixture was

cooled and the excess solvent was removed under reduced pressure. The mixture was extracted from water with chloroform several times, dried over magnesium sulphate, filtered and reduced in volume. The solid residue was subjected to column chromatography on alumina eluting with 95:5 chloroform/methanol mixture. The major band eluted from the column was reduced in volume and recrystallised from chloroform/hexane to yield 5,10,15-tris-(3,5-di-t-butyl-4-hydroxyphenyl)-20-(4-{4-nitrobenzyl}pyridiniumyl) porphyrinatomanganese bromide **33** as a green amorphous powder (0.092 mg, 74%). ( found: C, 69.25; H, 6.70; N, 6.08,  $C_{74}H_{81}N_6O_5MnBrCl \cdot C_6H_{14}$ . Requires: C, 69.07; H, 6.88; N, 6.04%).  $\lambda_{max}$  nm ( $\epsilon mol^{-1} dm^3 cm^{-1}$ ) 485 (105000), 593 (11300), 635 (16700).

FABS-MS (3-NOBA,  $CHCl_3$ ). Found:  $m/z = 1224, 1189, 1053$ ;  $[M-Br]^+$  requires  $m/z = 1224$ ;  $[(M-(Br^-)-(Cl)]$  requires  $m/z = 1189$ ;  $[(M-(Br) -(Cl)-(4-nitrobenzyl)]$  requires  $m/z = 1053$ .

Meso-5,10,15-tris(3,5-di-t-butyl-4-hydroxyphenyl)-20-(4-{4-bromomethylbenzyl} pyridiniumyl) porphyrinatomanganese bromide. - To an excess of  $MnCl_2 \cdot 4H_2O$  (1g,  $3.75 \times 10^{-4}$  mol) refluxing in DMF (30mls), porphyrin **27** (0.13g,  $1 \times 10^{-4}$  mol) was added and the mixture refluxed for 35 minutes. The reaction mixture was cooled, and reduced in volume under reduced pressure. The mixture was subjected to column chromatography on alumina eluting with 95.5 chloroform/methanol mixture. The first band eluted was the unreacted porphyrin, the second and major band eluted from the column was the desired 5,10,15-tris-(3,5-di-t-butyl-4-hydroxyphenyl)-20-(4-{4 bromomethylbenzyl} pyridiniumyl) porphyrinatomanganese bromide **34** as a green amorphous powder (0.069g, 53%).

(Found: C, 66.56; H, 6.16; N, 5.18.  $C_{75}H_{83}O_3N_5Br_2MnCl$  requires C, 66.59; H, 6.18; N, 5.18%).  $\lambda_{max}$  nm ( $\epsilon mol^{-1} dm^3 cm^{-1}$ ,  $CHCl_3$ ), 485.5 (120000), 592 (13000), 634 (18600).

FABS-MS (3 NOBA, CHCl<sub>3</sub>).

Found:  $m/z = 1352, 1272, 1157$ ,  $[M]^+$  requires  $m/z = 1352$ ,  $[M-Br]^+$  requires  $m/z = 1272$ ,  $[(M-(2Br)-(Cl))]$  requires  $m/z = 1157$ .

### **Metallation of porphyrin 30 with Zn, Co, Mn -**

meso-5,10,15-tris-(3,5-di-t-butyl-4-hydroxyphenyl)-20(4-{2-bromomethylbenzyl}porphyrinatomanganese dibromide. - To an excess of MnCl<sub>2</sub>.4H<sub>2</sub>O (1.5g,  $5.6 \times 10^{-3}$  mol) refluxing in DMF (30mls), porphyrin 30 (0.115g) was added and the mixture refluxed for one hour. The reaction mixture was cooled, and the solvent removed under reduced pressure. The mixture was extracted from water with chloroform, dried over magnesium sulphate, filtered and the solvent removed. The resulting residue was subjected to column chromatography on silica eluting with 50:50 chloroform/acetonitrile mixture. The major band was evaporated to dryness and recrystallised from chloroform/hexane to yield the desired meso-5,10,15-tris-(3,5-di-t-butyl-4-hydroxyphenyl)-20-(4-{2-bromomethylbenzyl}pyridiniumyl porphyrinato manganese dibromide 37 as a green/black solid (0.098mg, 63%). (Found : C, 63.01; H, 6.06; N, 5.11. C<sub>142</sub>H<sub>158</sub>N<sub>10</sub>O<sub>6</sub>MnBr<sub>2</sub>Cl<sub>2</sub>.CHCl<sub>3</sub>. Requires C, 63.34; H, 5.90; N, 5.11%).

$\lambda_{\max}$  nm ( $\epsilon$  mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>, CHCl<sub>3</sub>) 489.5 (190000), 594 (21000), 637(34300).

FABS-MS (3-NOBA, CHCl<sub>3</sub>), Found:  $m/z = 2442, 2362, 2290, 1052$ .  $[M+H]$  requires  $m/z = 2442$ ,  $[(M-(Br))]^+$  requires  $m/z = 2362$ ,  $[(M-(Br) - (Cl_2))]$  requires  $m/z = 2290$ ,  $[(M-2(Br) - (Cl_2) - (benzyl)-(porphyrin))]$  requires  $m/z = 1052$ .

Zinc and cobalt insertion was achieved by the addition of the metal acetate saturated in methanol to a refluxing solution of porphyrin 30 in chloroform. After 15 minutes the mixtures were cooled and reduced in volume. The porphyrin was extracted from water with chloroform, dried over magnesium sulphate, filtered and the solvent reduced by evaporation. The solid residues were subjected to column chromatography on silica eluting with 50:50



chloroform/acetonitrile mixture.

The band eluted to give the desired cobalt dimer was recrystallised from chloroform/hexane to yield a green/black solid **36** (0.12g, 77%). ( found: C, 69.02; H, 6.51; N, 5.62.  $C_{142}H_{158}N_{10}O_6Co_2Br_2 \cdot CHCl_3$ , requires C, 68.75; H, 6.42; N, 5.61 %.  $\lambda_{max}$  nm ( $\epsilon$  mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>, CHCl<sub>3</sub>) 438.5 (285000), 555 (33100), 599.5 (26800). FABS-MS (3-NOBA, CHCl<sub>3</sub>), Found  $m/z$  = 2298, 2218, 2113, 1058, [(M-Br)]<sup>+</sup> requires  $m/z$  = 2298; [(M-2(Br))]<sup>+</sup> requires  $m/z$  = 2218; [(M-2(Br) -(benzyl)) requires  $m/z$  = 2113); [(M-2(Br)) - (benzyl)-(porphyrin) ] requires  $m/z$  = 1058.

The band eluted to give the desired zinc dimer was also recrystallised from chloroform/hexane to yield a green/black solid **35** (0.132g, 83%) (found: C, 69.56; H, 6.75; N, 5.24.  $C_{142}H_{158}N_{10}O_6Br_2Zn_2 \cdot 4CH_3OH$ , requires C, 69.59; H, 6.96; N, 5.55%).  $\lambda_{max}$  nm ( $\epsilon$  mol<sup>-1</sup> dm<sup>3</sup>cm<sup>-1</sup>, CHCl<sub>3</sub>) 424 (305000), 562.5 (34400), 634.5 (35000). FABS-MS (3-NOBA, CHCl<sub>3</sub>), Found  $m/z$  = 2311, 2231, 1166, 1062. [(M-(Br))] requires  $m/z$  = 2311; [M-2(Br)] requires  $m/z$  = 2231; [(M-2(Br))- Zn porphyrin] requires  $m/z$  = 1166; [(M-2(Br)) -(benzyl)-(porphyrin) requires  $m/z$  = 1062.

### **Synthesis of 5,10,15,20-Tetrakis-(3,5-di-t-butyl-4-hydroxyphenyl) porphyrin**

5,10,15,20-tetrakis-(3,5-di-t-butyl-4-hydroxyphenyl) porphyrin 23 - Pyrrole (6.7g, 0.1 mol) was added to a refluxing solution of 3,5-di-t-butyl-4-hydroxybenzaldehyde (23.4g, 0.1 mol) in propionic acid (500 mls). Reflux was maintained for one hour thirty minutes, upon which the mixture was concentrated to one fifth of its original volume and cooled. The solid was filtered, taken into chloroform and subjected to column chromatography on alumina, eluting with chloroform. The major band eluted from the column was concentrated and crystallised from light petroleum to yield a purple powder **23** (3.8g, 13%).<sup>(1)</sup>

$\lambda_{\max}$  nm ( $\epsilon$  mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>, CH<sub>2</sub>Cl<sub>2</sub>) 426 (330000), 522 (14000), 560 (13000), 597 (5000), 654 (7000). FABS-MS (3NOBA, CHCl<sub>3</sub>) Found  $m/z$  = 1126 [M<sup>+</sup>] requires  $m/z$  = 1126. <sup>1</sup>H nmr  $\delta$ (ppm), 8.9 (s, 8H, pyrrole - $\beta$ -H), 8.1 (s, 8H, DtBHP ortho H), 5.6 (ss, 4H, phenolic OH), 1.72 (s, 72H, t-butyl H), - 2.63 (br s, 2H, porphyrin N-H).

### **Oxidation of Porphyrin 23**

#### 5,10,15,20-tetra-(3,5-di-t-butyl-4-oxacyclohexa-2,5-dienylene) porphyrinogen

Porphyrin 23, (500mg, 4.46 x 10<sup>-4</sup> mol) was stirred in chloroform (250 mls) with 10% (W/V) methanolic KOH for twentyfour hours. The solution was neutralised by adding a few drops of trifluoroacetic acid and the mixture was washed into a separating funnel with water. The lower organic layer was run off, dried over magnesium sulphate, filtered and reduced in volume by evaporation. The resulting solid residue was recrystallised from dichloromethane/light petroleum to yield dark green microcrystals 38<sup>(3)</sup> (300mg, 60%).

$\lambda_{\max}$  nm ( $\epsilon$  mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>, CH<sub>2</sub>Cl<sub>2</sub>) 508 (109000). FABS-MS (3-NOBA, CH<sub>2</sub>Cl<sub>2</sub>) Found  $m/z$  = 1124, [M<sup>+</sup>] requires  $m/z$  = 1124.

<sup>1</sup>H nmr  $\delta$  (ppm), 9.5 (br s, 2H, porphyrin N-H), 7.6 (s, 8H, pyrrole  $\beta$ -H), 6.8 (s, 8H, DtBHP ortho-H), 1.6 (s, 36H, t-butyl H), 1.3 (s, 36H, t-butyl-H).

### **N-Alkylation of the oxidised Porphyrin 38**

#### N-alkylation of 38 with 4-nitrobenzyl bromide in basified N,N'

Dimethylformamide - Porphyrinogen 38 (250mg, 2.2 x 10<sup>-4</sup> mol) was refluxed (3 hours) with 4-nitrobenzyl bromide (950 mg, 4.4 x 10<sup>-3</sup> mol) in N, N' - dimethylformamide (DMF) (50ml) basified with methanolic potassium hydroxide solution (1M, 10ml). After removal of the solvent by evaporation,

the solid residue was subjected to column chromatography on alumina, eluting with a 70:30 dichloromethane/petroleum spirit mixture. Two main bands were collected and their components identified as the tetra-N-4-nitrobenzyl porphyrinogen **39**<sup>(3)</sup> and the di-N-4-nitrobenzylporphyrinogen **40**<sup>(3)</sup>. The first band eluted from the column was evaporated to dryness and yielded the meso-5,10,15,20-tetrakis (3,5,-di-t-butyl-4-oxacyclohexa-2,5-dienylene)- N<sub>21</sub>, N<sub>22</sub>, N<sub>23</sub>, N<sub>24</sub> - tetra-4-nitro-benzylporphyrinogen **39** as a dark red amorphous powder (12mg, 3%). Yields of **39** were only enough for characterisation by UV/visible spectroscopy and FABS - mass spectrometry.  $\lambda_{\text{max}}$  nm ( $\epsilon$  mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>, CH<sub>2</sub>Cl<sub>2</sub>) 500 (96000). FABS-MS (3-NOBA, CHCl<sub>3</sub>) found  $m/z$  = 1667. [M + H] requires  $m/z$  = 1667.

The second band to be eluted was evaporated to dryness and crystallised from chloroform/petroleum spirit to yield the meso-5,10,13,20-tetrakis-(3,5-di-t-butyl-4-oxacyclohexa-2,5-dienylene) N<sub>21</sub>, N<sub>23</sub> -di-4-nitrobenzylporphyrinogen **40** as a dark green-black amorphous powder (150 mg, 48%).

$\lambda_{\text{max}}$  nm ( $\epsilon$  mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>, CHCl<sub>3</sub>) 503 (110000). FABS-MS (3-NOBA, CHCl<sub>3</sub>) found:  $m/z$  = 1396 [M<sup>+</sup>] requires  $m/z$  1396.

<sup>1</sup>H nmr (ppm, CDCl<sub>3</sub>) 9.90 (br s, 2H, N-H), 8.08, 7.97, 6.83, 6.72 (pair of doublets, 8H, 4-nitrobenzyl-H, J<sub>AB</sub> = 8.4Hz), 7.58 (s, 4H, pyrrole  $\beta$ -H on N-alkylated ring), 7.19 (s, 4H, pyrrole  $\beta$ -H on non-alkylated pyrrole ring), 6.69 (s,8H, DtBHP ortho H on 3,5-di-t-butyl-4-oxyacyclohexa-2,5-dienylene groups), 4.64 (br s, 4H, 4-nitrobenzylic - CH<sub>2</sub>-), 1.3 (complex s, 72H, t-butyl-H).

N- Alkylation of **38** with 4-nitrobenzylbromide in acetonitrile basified with caesium carbonate - Porphyrinogen **38** (250mg, 2.2x10<sup>-4</sup> mol) was refluxed (3 hours) with 4-nitrobenzylbromide (950 mg, 4.4x10<sup>-3</sup> mol) in dry acetonitrile (50ml) basified with caesium carbonate (1g). After removal of solvent by evaporation the solid residue was subjected to column chromatography on alumina, eluting with dichloromethane/petroleum spirit (70:30). The major

component (first band) to be eluted from the column was evaporated to dryness and recrystallised from dichloromethane/petroleum spirit to yield the meso - 5,10,15,20-tetrakis (3,5-di-t-butyl-4-oxacyclohexa-2, 5-dienylene) - N<sub>21</sub>, N<sub>22</sub>, N<sub>23</sub>, N<sub>24</sub> - tetra-4-nitrobenzyl porphyringen **39** as a dark red amorphous powder (190 mg, 49%). ( found: C, 74.29; H, 6.64; N, 6.73. C<sub>104</sub>.H<sub>112</sub>.N<sub>8</sub>O<sub>12</sub>.½H<sub>2</sub>O requires C, 74.57; H, 6.79; N, 6.69%).  $\lambda_{\max}$  nm ( $\epsilon$  mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>, CHCl<sub>3</sub>) 500 (96000). FABS- MS (3-NOBA, CHCl<sub>3</sub>) found:  $m/z$  = 1666, [M]<sup>+</sup> requires  $m/z$  = 1666. <sup>1</sup>H nmr  $\delta$ (ppm, CDCl<sub>3</sub>) 8.106, 8.062, 6.839, 6.796 (pair of doublets, 16H, 4-nitrobenzyl-H, J<sub>AB</sub> = 8.6 Hz), 7.21 (s, 8H, pyrrole  $\beta$ -H), 6.74 (s, 8H, Ortho-H on 3, 5-di-t-butyl-4 oxacyclohexa - 2,5-dienylene group), 4.62 (br s, 8H, 4-nitrobenzylic - CH<sub>2</sub>), 1.24 (s, 72H, t-butyl-H).

N-Alkylation of **38** with  $\alpha,\alpha'$ -di-bromo-*p*-xylene in acetonitrile basified with caesium carbonate - Porphyringen **38** (250 mg, 2.2 x 10<sup>-4</sup> mol) was refluxed (3 hours) with  $\alpha,\alpha'$ -di-bromo-*p*-xylene (1.16g, 4.4 x 10<sup>-3</sup> mol) in dry acetonitrile (50ml) basified with caesium carbonate (1g). After removal of solvent by evaporation, the solid residue was subjected to column chromatography on alumina, eluting with dichloromethane/petroleum spirit (70:30). One major band was eluted and on evaporation and crystallisation from dichloromethane/hexane yielded the meso-5,10,15,20-tetrakis-(3,5,-di-t-butyl-4-oxacyclohexene-2,5-dienylene) N<sub>21</sub>, N<sub>22</sub>, N<sub>23</sub>, N<sub>24</sub> - tetra-bromomethylbenzyl porphyrinogen **41** as a red amorphous powder (160 mg, 39%). (Found C, 67.54; H, 6.67; N, 2.49. C<sub>108</sub> H<sub>120</sub> N<sub>4</sub> O<sub>4</sub> Br<sub>4</sub>.4-MeOH requires C, 67.73; H, 6.90; N, 2.82 %).  $\lambda_{\max}$  nm ( $\epsilon$  mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>, CHCl<sub>3</sub>) 491 (110000). FABS-MS (3-NOBA, CHCl<sub>3</sub>) found 1859, 1857, 1778, [M+2H<sup>+</sup>] requires  $m/z$  = 1859, [M]<sup>+</sup> requires  $m/z$  = 1857, [M-Br<sup>-</sup>] requires  $m/z$  = 1778. <sup>1</sup>H nmr  $\delta$  ( ppm, CDCl<sub>3</sub>) 7.221, 7.181, 6.049, 6.609 (pair of doublets, 16H; 4-bromomethylbenzyl-H, J<sub>AB</sub> = 8 Hz), 7.37 (s, 8H, pyrrole  $\beta$ -H), 5.16 (s, 8H, ortho-H on 3,5-di-t-butyl-4-oxacyclohexa-2,5-dienylene group), 4.48 (s, 8H, 4-bromomethylbenzyl-CH<sub>2</sub>), 4.35 (s, 8H, CH<sub>2</sub>Br), 1.25 (s, 72H, t-butyl-H).

Reduction of compound **39** with tin (II) chloride and hydrochloric acid.

Meso-5,10,15,20-tetrakis-(3,5-di-t-butyl-4-oxacyclohexa-2,5-dienylene)-N<sub>21</sub>, N<sub>22</sub>, N<sub>23</sub>, N<sub>24</sub>-4-nitrobenzylporphyrinogen **39** (1g, 6x10<sup>-4</sup> mole) was taken into a small amount of chloroform (50 ml). Concentrated hydrochloric acid (50 ml) was added, and the mixture degassed with nitrogen. A nitrogen-degassed solution of tin (II) chloride (4-5g) in hydrochloric acid (70ml) was added dropwise to the mixture and heated in a water bath (75-80°C) for 3-4 hours. The mixture was cooled, neutralised with the slow addition of 60ml of concentrated ammonium hydroxide (ensuring a low temperature is maintained). The resultant basic solution was exposed to air and filtered. The solid residue was stirred in 5% sodium hydroxide (200ml), filtered, washed with water and dried to yield the desired meso-5,10,15,20-tetrakis-(3,5-di-t-butyl-4-oxacyclohexa-2, 5-dienylene) - N<sub>21</sub>, N<sub>22</sub>, N<sub>23</sub>, N<sub>24</sub>-tetra-4-aminobenzyl porphyrinogen **42** (300 mg, 33% ).

$\lambda_{\max}$  nm ( $\epsilon$  mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>, CH<sub>3</sub>Cl) 508 (110000). FABS-MS (3-NOBA, CH<sub>2</sub>Cl<sub>3</sub>). Found 1547, [ M+H] requires m/z = 1547. <sup>1</sup>Hnmr  $\delta$ (ppm, CDCl<sub>3</sub>) 7.24 (s, 8H, pyrrole  $\beta$ -H), 6.65 (s, 8H, ortho-H on 3,5-di-t-butyl-4-cyclohexa-2, 5-dienylene group), 6.44 (s, 16H, 4 aminobenzylic H), (br s, 8H, 4-aminobenzylic-CH<sub>2</sub>), 4.34 (br s, 8H, N-H), 1.26 (complex s, 72H, t-butyl-H). D<sub>2</sub>O exchange shows the loss of the peak at 4.34 indicating the disappearance of the NH<sub>2</sub> group. Infrared analysis also confirms we have the desired product with the characteristic N-H stretch in the region of 3500cm<sup>-1</sup>. The C-H stretches are observed at 3000cm<sup>-1</sup>, 2990cm<sup>-1</sup>, C=O stretch at 1601cm<sup>-1</sup> and the C-N stretch at 1720cm<sup>-1</sup>. The absence of any stretches in the NO<sub>2</sub> region of the spectra indicates that the reaction has gone to completion and the tetra amino is the desired product.

## Synthesis of a tetra- (arylethynyl) porphyrin

4-Dodecyloxybenzaldehyde - 4-hydroxybenzaldehyde (10g, 0.08 mole), dodecylbromide (24.5g, 0.1 mole), and potassium carbonate (28.2g, 0.2 mole) were stirred in DMF (100ml) and heated to 80-90°C under nitrogen for five hours. On completion the mixture was cooled to room temperature and poured into a large volume of iced water (800 ml). The aldehyde was extracted with several portions of diethylether which was then washed with several portions of water saturated with sodium chloride. The layers were separated and the ether layer was dried over magnesium sulphate, filtered and reduced in volume to give an oily residue. This was triturated with methanol to give a white solid which was filtered and dried to yield the desired 4-dodecyloxybenzaldehyde **43** (14.3g, 61%). Mpt. 23-26°C. MS (EI): Found  $m/z = 290$ ,  $[M^+]$  requires  $m/z = 290$ .

$^1\text{Hnmr}$   $\delta$  (ppm,  $\text{CDCl}_3$ ), 9.88 (s, 1H, aldehyde-H), 7.841, 7.818, 7.005, 6.980 (quartet, 4H, aromatic-H, AB spin system,  $J_{AB} = 8.28$  Hz), 4.06, 4.04, 4.02 (t, 2H,  $\text{OCH}_2\text{CH}_2$ ), 1.85, 1.83, 1.81, 1.79 (q, 2H,  $\text{OCH}_2\text{CH}_2\text{CH}_2$ ), 1.50, 1.48, 1.46, 1.44, 1.42 (p, 2H,  $\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.42 (complex s, 16H,  $-\text{[CH}_2\text{]}_8$ ), 0.90, 0.88, 0.86 (t, 3H,  $\text{CH}_2\text{CH}_3$ ).

4-Dodecyloxyphenyldibromostyrene<sup>(4)</sup> - To a solution of carbon tetrabromide (11.5g, 0.035 mol) in dichloromethane (50ml), zinc dust (2.26g, 0.035 mol) and triphenylphosphine (9.03g, 0.035 mole) were added slowly and the temperature of the reaction controlled by the use of an ice-bath. The mixture was sealed under nitrogen, brought to room temperature and left to stir for twelve hours. The previously made aldehyde **43** (5g, 0.0175 mol) was added slowly to the mixture, again the temperature being controlled by an ice-bath. The reaction mixture was sealed under nitrogen and stirred at room temperature whilst continuously being monitored by TLC. On completion, the reaction mixture was poured into a large stirred volume of pentane (600-800

ml), producing a precipitate. The precipitate was filtered and the pentane layer was concentrated to give a white solid. This solid was subjected to column chromatography on silica eluting with dichloromethane/petroleum spirit (30:70) to yield the desired  $\beta,\beta$ -dibromostyryl derivative **44** as a white solid (6.6g, 86%).

MS (EI): Found  $m/z = 446$ ,  $[M^+]$  requires  $m/z = 446$ .  $^1\text{H}$  nmr  $\delta$ (ppm,  $\text{CDCl}_3$ ), 7.509, 7.485, 6.888, 6.864 (quartet, 4H, AB spin system for aromatics,  $J_{AB} = 8.64$  Hz), 7.40 (s, 1H,  $\text{CH} = \text{CBr}_2$ ), 3.97, 3.96, 3.94 (t, 2H,  $\text{CH}_2$  next to the oxygen group), 1.79-1.75 (m, 2H,  $\text{C}_2$   $\text{OCH}_2\text{CH}_2\text{CH}_2$ ), 1.46 - 1.42 (m, 2H,  $\text{CH}_2\text{CH}_3$ ), 1.30 (m, 16H, rest of  $[\text{CH}_2]_8$  chain), 0.90, 0.88, 0.86 (t, 3H,  $\text{CH}_2\text{CH}_3$ ).

#### 4-Dodecyloxyphenyl propynal<sup>(5)</sup> - The $\beta,\beta$ -dibromostyryl derivative **44**

(5.8 gm, 0.013 mol) was dissolved in dry THF (60-80ml), sealed under nitrogen and the reaction temperature lowered to  $-78^\circ\text{C}$  (cardice/acetone bath). BuLi (20.3mls, 0.0325 mole) was added dropwise to the solution and the mixture was stirred at  $-78^\circ\text{C}$  for two hours. Dimethyl formamide (2ml) was added and the mixture was allowed to warm to room temperature and was left for a further hour. The mixture was poured into a stirred flask of iced water (600 ml) acidified with concentrated hydrochloric acid (5ml). The pH of the solution was increased to pH 6-7 by the slow addition of a saturated solution of sodium carbonate, ensuring the pH did not rise above pH 8. The product was extracted with several portions of diethyl ether, dried over magnesium sulphate, filtered and reduced in volume to give a yellow/ brown oil. The oily residue was subjected to column chromatography on silica eluting with dichloromethane/petroleum spirit (30:70). The eluted band was reduced in volume by evaporation to yield the desired 4-dodecyloxyphenylpropynal **45** as a yellow solid (2.61gm, 64%).

MS (EI): Found  $m/z = 314$ ,  $[M^+]$  requires  $m/z = 314$ .  $^1\text{H}$  nmr  $\delta$  (ppm,  $\text{CDCl}_3$ ). 9.40 (s, 1H,  $\text{CHO}$ ), 7.563, 7.538, 6.911, 6.886 (quartet, 4H, AB spin for aromatic,  $J_{\text{AB}} = 9$  Hz), 4.01, 3.99, 3.97 (t, 2H,  $\text{OCH}_2\text{CH}_2\text{CH}_2$ ), 1.83, 1.81, 1.79, 1.77, 1.76 (p, 2H,  $\text{CH}_2\text{CH}_2$  near the oxygen group), 1.47 - 1.36 (m, 2H,  $\text{CH}_2$  next to terminal  $\text{CH}_3$ ), 1.3 - 1.2 (complex s, 16H,  $-\text{[CH}_2\text{]}_8$ ), 0.90, 0.88, 0.86 (t, 3H,  $\text{CH}_2\text{CH}_3$ ).

4-Dodecyloxyphenylethynyldipyrromethane - Pyrrole (5.3g, 0.08 mole) and the previously synthesised arylpropynal **45** (0.5g,  $1.59 \times 10^{-3}$  mole) were weighed into a three-necked round bottomed flask and bubbled with nitrogen for ten minutes. The flask was sealed under nitrogen and the reaction temperature was lowered to  $-25^\circ\text{C}$  (cardice/carbon tetrachloride). A catalytic amount of  $\text{BF}_3 \cdot \text{OET}_2$  (65  $\mu\text{l}$ ,  $5.3 \times 10^{-4}$  mole) was added and the reaction mixture allowed to stir for thirty minutes. Dichloromethane (50ml) was added to the mixture and then washed with two portions of sodium hydroxide (50ml, 0.1M). The organic layer was then washed several times with water, dried over sodium sulphate, filtered and reduced in volume to give a brown oil. This was immediately subjected to column chromatography on silica eluting with cyclohexane/ethyl acetate/triethylamine (80:19:1). Several minor bands were eluted but not analysed. The major band to be eluted was concentrated to give the desired dipyrromethane **46** as a brown solid (0.48gm, 71%). MS. (EI): Found  $m/z = 430$ ,  $[M^+]$  requires  $m/z = 430$ .  $^1\text{H}$  nmr  $\delta$  (ppm,  $\text{CDCl}_3$ ), 8.23 (broad s, 2H, N-H), 7.395, 7.371, 6.840, 6.816 (quartet, 4H, AB spin system for aromatics.  $J_{\text{AB}} = 8.64\text{Hz}$ ), 6.73, 6.71, 6.19, 6.18, (two doublets, 6H, pyrrole  $\beta\text{-H}$ ), 5.38 (s, 1H, methane bridge H), 3.97, 3.95, 3.93 (t, 2H,  $\text{OCH}_2\text{CH}_2$ ), 1.81, 1.79, 1.77, 1.75, 1.73 (p, 2H,  $\text{OCH}_2\text{CH}_2\text{CH}_2$ ), 1.47, - 1.42 (m, 2H,  $\text{CH}_2\text{CH}_3$ ), 1.26 (m, 16H,  $[\text{CH}_2]_8$ ), 0.90, 0.88, 0.86 (t, 3H,  $\text{CH}_2\text{CH}_3$ ).

5,10,15,20-meso-Tetra-(4-dodecyloxyphenylethynyl)porphyrin - Boron trifluoride diethyletherate (55  $\mu\text{l}$ ,  $3.91 \times 10^{-4}$  mol) was added to a stirred, nitrogen degassed solution of 4-dodecyloxyphenylpropynal **45** (0.37g,  $1.18 \times 10^{-3}$  mol) and 4-dodecyloxyphenylethynyl dipyrromethane **46**



(0.5g,  $1.10 \times 10^{-3}$  mol) in dry, distilled dichloromethane (120ml) at  $-25^{\circ}\text{C}$ . The reaction mixture was kept at this temperature for three hours, then allowed to warm to room temperature overnight. DDQ (266mg,  $1.16 \times 10^{-3}$  mol) was added, resulting in the solution turning green. The solvent was removed under vacuum, and the resulting residue subjected to column chromatography on silica eluting with dichloromethane to give a dark green sticky solid. Trituration with methanol and filtration gave the desired porphyrin 47 as a dark green powder (0.13g, 15%). m.pt.  $124^{\circ}\text{C}$ . (found: C, 82.76; H, 8.90; N, 3.75,  $\text{C}_{100}\text{H}_{120}\text{N}_4\text{O}_4$  requires C, 82.94; H, 8.77; N, 3.87%).  $\lambda_{\text{max}}$  nm ( $\epsilon \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ , DCM) 473 (290000), 655 (90200), 745 (54300). FABS-MS (3-NOBA,  $\text{CHCl}_3$ ) Found  $m/z = 1448$ ,  $[\text{M}^+]$ ; requires  $m/z = 1448$ .  $^1\text{H}$  nmr  $\delta$ (ppm,  $\text{CDCl}_3$ ), 9.13 (s, 8H, pyrrole  $\beta$ -H); 7.921, 7.897, 7.073, 7.049 (quartet, 16H, AB spin system from aromatic H,  $J_{\text{AB}} = 8.64 \text{ Hz}$ ), 4.09, 4.07, 4.06 (t, 8H,  $\text{OCH}_2\text{CH}_2$ ), 1.92, 1.90, 1.88, 1.86, 1.84 (p, 8H,  $\text{OCH}_2\text{CH}_2\text{CH}_2$ ), 1.52-1.41 (m, 8H,  $\text{CH}_2\text{CH}_3$ ), 1.31 (broad s, 64H,  $[\text{CH}_2]_8$ ), 0.91, 0.87, 0.85 (t, 12H,  $\text{CH}_2\text{CH}_2$ ), -2.89 (broad s, 2H, porphyrin N-H).

5,10,15,20-meso-Tetra-(4-dodecyloxyphenylethynyl)porphyrinatozinc -

Porphyrin 47 (0.08 gm,  $5.525 \times 10^{-5}$  mol) was dissolved in chloroform (25ml) and warmed in a water bath to  $50\text{-}60^{\circ}\text{C}$ . A saturated solution of zinc acetate in methanol was added slowly and the reaction was monitored by UV/visible spectroscopy. On completion of the reaction, the solvent was removed under pressure and the residue was subjected to column chromatography on silica eluting with dichloromethane. The resulting band eluted from the column was concentrated and triturated with methanol to yield a green solid which was filtered and washed with methanol. The resulting green solid was the desired 5,10,15,20-meso-tetra-(4-dodecyloxyphenylethynyl) porphyrinato zinc 48 (0.07g, 85%). (m.pt.  $135^{\circ}\text{C}$ ).

$\lambda_{\text{max}}$  nm ( $\epsilon \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ ),  $\text{CH}_2 \text{ Cl}_2$  ) 483 ( 253000), 635 ( 15000 ), 689 (43000 ). FABS-MS (3-NOBA,  $\text{CHCl}_3$ ). Found  $m/z = 1511$  ,  $[\text{M}]$  requires  $m/z = 1511$ .  $^1\text{H}$ nmr  $\delta$ (ppm,  $\text{CDCl}_3$ ) 9.11 (s, 8H, pyrrole  $\beta$ -H), 7.89, 7.87, 7.06, 7.04 (quartet, 16H, AB Spin system from aromatic H,  $J_{\text{AB}} = 8.64 \text{ Hz}$ ),

4.05, 4.03, 4.01 (t, 8H, OCH<sub>2</sub>CH<sub>2</sub>), 1.90-1.85 (m, 8H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.54-1.49 (m, 8H, CH<sub>2</sub>CH<sub>3</sub>), 1.30 (broad s, 64H, [CH<sub>2</sub>]<sub>8</sub>), 0.91, 0.89, 0.88 (t, 12H, CH<sub>2</sub>CH<sub>3</sub>).

5,10,15,20-meso-Tetra-(4-dodecyloxyphenylethynyl)porphyrinatocopper-  
Porphyrin **47** (0.1g,  $6.91 \times 10^{-5}$  mole) was dissolved in chloroform (25ml) and warmed in a water bath to 50-60°C. A saturated solution of copper acetate in methanol was slowly added and the reaction monitored by UV/visible spectroscopy and TLC. After 10 minutes the reaction was stopped and the solvent removed under pressure. The mixture was extracted from water with dichloromethane several times, dried over magnesium sulphate, filtered and reduced in volume. The solid residue was subjected to column chromatography on silica, eluting with dichloromethane/hexane (70:30). The major band eluted was reduced in volume, triturated in methanol and filtered to yield the desired 5,10,15,20-meso-tetra-(4-dodecyloxyphenylethynyl) porphyrinato copper **49** as a green solid (0.087g, 83%), mpt. 115-118°C. (found: C, 79.66; H, 9.06; N, 3.12, C<sub>100</sub> H<sub>124</sub>N<sub>4</sub>O<sub>4</sub>.1.5C<sub>6</sub>H<sub>14</sub>. requires: C, 79.88; H, 8.92; N, 3.41%).  $\lambda_{\max}$  nm ( $\epsilon$  mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>, CH<sub>2</sub>Cl<sub>2</sub>) 478 (239000), 620 (10700), 666 (36000). FABS-MS (3NOBA, CHCl<sub>3</sub>) found  $m/z$  = 1510, 1511, [M+H] requires  $m/z$  = 1510 and [M+2H] requires  $m/z$  = 1511.

5,10,15,20-meso-Tetra-(4-dodecyloxyphenylethynyl)porphyrinato nickel-  
Porphyrin **47** (0.01 gm,  $6.91 \times 10^{-5}$  mole) was brought to reflux in DMF (30ml) and NiCl<sub>2</sub>.H<sub>2</sub>O was added in small amounts and the reaction was followed by UV/Visible spectroscopy and TLC. After twenty-five minutes the reaction was stopped, cooled down and the solvent removed under pressure. The mixture was extracted from water with several portions of dichloromethane, dried over magnesium sulphate, filtered and reduced in volume. The solid residue was subjected to column chromatography on silica, eluting with dichloromethane/hexane (70:30). The major band eluted was reduced in volume, triturated in methanol and filtered to yield the desired 5,10-15,20-meso-tetra-(4-dodecyloxyphenylethynyl) porphyrinato-nickel **50** as a green solid

(0.68gm, 65%) m.pt.-103°C. (found:C, 80.07; H, 8.49; N, 3.67%).

$C_{100}H_{124}N_4O_4.C_6H_{14}$  requires C, 80.02; H, 8.74; N, 3.52%).  $\lambda_{max}$  nm  
( $\epsilon$  mol<sup>-1</sup>dm<sup>3</sup> cm<sup>-1</sup>, CH<sub>2</sub>Cl<sub>2</sub>) 476 (236.7), 597 (15), 648 (38.8).

FABS-MS (3-NOBA,CHCl<sub>3</sub>) found  $m/z = 1505$ , [M+H] requires  $m/z = 1505$ .

<sup>1</sup>H nmr  $\delta$  (ppm, CDCl<sub>3</sub>) 8.96 (s, 8H, pyrrole  $\beta$ -H), 7.79, 7.76, 6.99, 6.97  
(quartet, 16H, AB spin system of phenyl H,  $J_{AB} = 8.64$  Hz), 4.05, 4.03, 4.01 (t,  
8H, OCH<sub>2</sub>CH<sub>2</sub>), 1.89-1.83 (s, 8H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.31-1.28 (s, 8H,  
CH<sub>2</sub>CH<sub>3</sub>), 1.26 (complex singlet, 64H, [CH<sub>2</sub>]<sub>8</sub>), 0.91, 0.89, 0.88 (t, 12H, CH<sub>2</sub>  
CH<sub>3</sub>).

5,10,15,20-meso-Tetra-(4-dodecyloxyphenylethynyl) porphyrinato palladium -

Porphyrin 47 (0.01g,  $6.91 \times 10^{-5}$  mole) and palladium acetate (0.016g ) were  
gently refluxed in a chloroform/methanol mixture (5:1) for two hours. A slight  
excess of palladium acetate was added and the mixture was allowed to reflux  
for a further thirty minutes. The reaction was monitored throughout by TLC  
and UV/visible spectroscopy. The reaction was stopped, allowed to cool and  
the solvent was removed under pressure. The resulting solid residue was  
subjected to column chromatography on silica, eluting with  
dichloromethane/hexane (70:30). The major band eluted was reduced in  
volume, triturated in methanol and filtered to yield the desired 5,10,15,20-  
meso-tetra-(4-dodecyloxyphenylethynyl) porphyrinato palladium 51 as a green  
solid (0.035gm, 33%) m.pt. 80-90°C. (Found C, 75.78; H, 7.94; N, 3.22.  
 $C_{100}H_{124}N_4O_4Pd.CH_3OH$  requires C, 75.88; H, 8.12; N, 3.47%).  $\lambda_{max}$  nm ( $\epsilon$   
mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup> CH<sub>2</sub>Cl<sub>2</sub>) 475 (267000 ), 593 ( 18000), 644 (53000 ). FABS-  
MS (3-NOBA, CHCl<sub>3</sub>) found:  $m/z = 1553$ , [M]<sup>+</sup> requires  $m/z = 1553$ . <sup>1</sup>H nmr  $\delta$   
(ppm, CDCl<sub>3</sub>) 8.70 (s, 8H, pyrrole  $\beta$ -H), 7.80, 7.78, 6.97, 6.95 (quartet, 16H,  
AB spin from phenyl H,  $J_{AB} = 8.64$ Hz), 4.05, 4.03, 4.01 (t, 8H, OCH<sub>2</sub>CH<sub>2</sub>),  
1.93-1.87 (m, 8H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.54-1.48 (m, 8H, CH<sub>2</sub>OCH<sub>3</sub>), 1.26  
(complex s, 64H, [CH<sub>2</sub>]<sub>8</sub>), 0.95, 0.93, 0.91 (t, 12H, CH<sub>2</sub>CH<sub>3</sub>).

5,10,15,20-meso-Tetra(4-dodecyloxyphenylethynyl)porphyrinato manganese -  
Porphyrin 47 (0.1g,  $6.91 \times 10^{-5}$  mole) was brought to reflux in DMF (30ml) and  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  was added in small amounts. The reaction was followed by TLC and UV/visible spectroscopy and the reaction was stopped after thirty minutes, cooled and the excess solvent removed under vacuum. The mixture was extracted from water with dichloromethane, dried over magnesium sulphate, filtered and reduced in volume. The solid residue was subjected to column chromatography eluting with chloroform/hexane (70:30). The major band eluted was reduced in volume, triturated in methanol and filtered to yield the desired 5,10,15,20-mesotetra-(4-dodecyloxyphenylethynyl) porphyrinato manganese 52 as a green solid (0.058g, 56%). m.pt. 205-206°C. (found: C, 76.83; H, 8.08; N, 3.62.  $\text{C}_{100}\text{H}_{124}\text{N}_4\text{O}_4\text{Mn} \cdot \text{Cl} \cdot 2\text{MeOH}$  requires C, 76.63; H, 8.20; N, 3.50%).  $\lambda_{\text{max}}$  nm ( $\epsilon \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ ,  $\text{CH}_2\text{Cl}_2$ ) 458 (109000), 513 (189000), 730 (66000). FABS-MS (3NOBA,  $\text{CHCl}_3$ ) found:  $m/z = 1501, 1502$ , [M] requires  $m/z = 1501$  and [M+H] requires  $m/z = 1502$ .

2-Bromo-5,10,15,20,meso-Tetra-(4dodecyloxyphenylethynyl) porphyrin

Porphyrin 47 (0.015g,  $1.04 \times 10^{-4}$  mol) was dissolved in carbon tetrachloride (30ml) and stirred at 0°C. Pyridine (1ml) and N-bromosuccinimide (0.22gm,  $1.25 \times 10^{-4}$  mol) were added to the porphyrin and the mixture was allowed to stir at 0°C, eliminating all sources of light. The reaction was followed by tlc and after thirty minutes the reaction was stopped. The excess solvent was removed under vacuum, and then washed with water with the organic layer being removed with dichloromethane. The organic layer was dried over magnesium sulphate, filtered and reduced in volume to give a green solid residue. The residue was subjected to column chromatography on silica eluting with dichloromethane/cyclohexane (60:40) and three main bands were eluted. The first band eluted from the column was reduced in volume to yield a green solid, but there was insufficient sample to carry out conclusive analysis. The second, and major band eluted from the column, yielded the 2-bromo-5,10,15,20-mesotetra-(4-dodecyloxyphenylethynyl) porphyrin 53 as a green solid (0.074g, 47%). m.pt. 65-67°C  $\lambda_{\text{max}}$  nm ( $\epsilon \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ ,  $\text{CH}_2\text{Cl}_2$ ), 468

(459000), 633 (99000), 724 (59000). FABS-MS (3NOBA, CH<sub>2</sub>Cl<sub>2</sub>) found:  $m/z = 1528, 1448$ , [M+H]<sup>+</sup> requires  $m/z = 1528$ , [M-Br]<sup>+</sup> requires  $m/z = 1448$ .

<sup>1</sup>H nmr  $\delta$  (ppm, CDCl<sub>3</sub>) 9.66, 9.64 (d, 2H,  $\beta$ -pyrrolic-H<sub>7,8</sub>), 9.47 (br s, 3H,  $\beta$ -pyrrolic-H<sub>13,17,18</sub>), 9.36, 9.34 (d, 2H,  $\beta$ -pyrrole-H<sub>12,13</sub>), 8.062, 8.052, 7.206, 7.182 (AB spin system, 4H, aromatic-H on C<sub>20</sub>, J<sub>AB</sub>=8.64 Hz), 7.969, 7.947, 7.103, 7.081 (AB spin system, 4H, aromatic-H on C<sub>5</sub>, J<sub>AB</sub> = 8.64 Hz), 7.931, 7.907, 7.101, 7.077 (AB spin system 8H, aromatic-H on C<sub>10,15</sub>, J<sub>AB</sub> = 8.64 Hz), 4.12, 4.10, 4.08 (t, 8H, OCH<sub>2</sub>CH<sub>2</sub>), 1.92, 1.91, 1.87, 1.86, 1.83 (p, 8H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.42-1.37 (m, 8H, CH<sub>2</sub>CH<sub>2</sub>), 1.25 (complex s, 64H, [CH<sub>2</sub>]<sub>8</sub>), 0.92, 0.90, 0.88 (t, 12H, CH<sub>2</sub>CH<sub>3</sub>), - 1.63 (br s, 2H, porphyrin N-H).

### Synthesis of arylethynyl porphyrins using protection chemistry -

#### 4-Dodecyloxyphenyl Co<sub>2</sub>(CO)<sub>6</sub>-ethynyl-protected aldehyde 15<sup>(6)</sup> -

4-Dodecyloxyphenylpropynal **45** (0.25g, 7.96 x 10<sup>-4</sup> mol) was added to a solution of Co<sub>2</sub>(CO)<sub>8</sub> (0.27g, 7.96 x 10<sup>-4</sup> mol) in tetrahydrofuran (10ml) and left to react under nitrogen, at room temperature until the effervescence of CO ceased. The reaction was stopped after thirty minutes and the excess solvent removed under vacuum to yield a brown solid residue which was columned on silica gel eluting with dichloromethane/petroleum spirit (30:70). The major band eluted from the column was concentrated to give the Co<sub>2</sub>(CO)<sub>6</sub> protected aldehyde **54** (0.41g, 86%) as a chocolate brown solid. ( found: C, 53.92; H, 5.29; C<sub>27</sub>H<sub>30</sub>O<sub>8</sub>Co<sub>2</sub> requires C, 54.01; H, 5.29 %). IR - loss of the characteristic ethynyl band at 2196 cm<sup>-1</sup> and the appearance of terminal carbonyl groups centred on 2062 cm<sup>-1</sup>. <sup>1</sup>H nmr  $\delta$ (ppm, CDCl<sub>3</sub>) 10.51 (s, 1H, aldehyde - H), 7.545, 7.521, 6.892, 6.868 (AB spin quartet, 4H, phenyl-H. J<sub>AB</sub> = 8.64 Hz), 3.99, 3.98, 3.96 (t, 2H, OCH<sub>2</sub>CH<sub>2</sub>), 1.82-1.76 (m, 2H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.46-1.42 (m, 2H, CH<sub>2</sub>CH<sub>3</sub>), 1.26 (complex singlet, 16H, [CH<sub>2</sub>]<sub>8</sub>), 0.89, 0.88, 0.86, (t, 3H, CH<sub>2</sub>CH<sub>3</sub>).

### 5,10,15,20-meso-Tetra[Co<sub>2</sub>(CO)<sub>6</sub>-ethynyl-protected] porphyrin

Aldelyde **54** (0.275g,  $4.58 \times 10^{-4}$  mol) and pyrrole (0.031g,  $4.58 \times 10^{-4}$  mol) were dissolved in dry dichloromethane (40ml) and degassed with nitrogen for ten minutes. The reaction was sealed under nitrogen, the reaction temperature reduced to  $-25^{\circ}\text{C}$ , shielded from the light and left for ten minutes.  $\text{BF}_3 \cdot \text{OET}_2$  (19 $\mu\text{l}$ ,  $1.52 \times 10^{-4}$  mole) was added and the reaction was left for twelve hours. DDQ (0.08g,  $3.52 \times 10^{-4}$  mol) was added and the dichloromethane removed under vacuum to yield a red/brown solid residue which was subjected to column chromatography on silica eluting with petroleum spirit/dichloromethane (70:30). The first and major band to be eluted from the column was reduced in volume to yield the  $\text{Co}_2(\text{CO})_6$  protected porphyrin **55** (0.087g, 30%) as a chocolate brown solid. (found: C, 59.57; H, 6.02; N, 1.96,  $\text{C}_{124}\text{H}_{126}\text{N}_4\text{O}_{28}\text{Co}_8 \cdot 3\text{C}_6\text{H}_{14}$  requires C, 59.85; H, 5.90; N, 1.97%).

$^1\text{H}$  nmr  $\delta$ (ppm,  $\text{CDCl}_3$ ) 9.02 (br s, 8H, pyrrolic  $\beta$ -H), 7.293, 7.270, 6.776, 6.753 (AB spin quartet, 16H, aromatic H,  $J_{\text{AB}} = 8.28$  Hz), 3.94, 3.93, 3.91 (t, 8H,  $\text{OCH}_2\text{CH}_2$ ), 1.80-1.78 (complex s, 8H,  $\text{OCH}_2\text{CH}_2\text{CH}_2$ ), 1.44-1.40 (complex s, 8H,  $\text{CH}_2\text{CH}_3$ ), 1.27 (complex br s, 64H,  $[\text{CH}_2]_8$ ), 0.88, 0.86, 0.84 (t, 12H,  $\text{CH}_2\text{CH}_3$ ), - 2.92 (br s, 2H, porphyrin N-H).

### **Deprotection of porphyrin 55**

The  $\text{Co}_2(\text{CO})_6$ -protected porphyrin (0.05g,  $1.92 \times 10^{-5}$  mol) was dissolved in dichloromethane (25ml) and transferred to a separating funnel. To this an excess of iron (III) perchlorate dissolved in methanol was added and the mixture was shaken at room temperature several successive times to produce a green solution. This was extracted from water, dried over magnesium sulphate, filtered, reduced in volume and subjected to column chromatography on silica gel eluting with dichloromethane. The major band eluted from the column was reduced in volume to yield the 5,10,15,20-mesotetra-(4-dodecyloxyphenylethynyl) porphyrin **47** as a green solid (12mg, 43%). Characterisation is identical to that previously reported for this porphyrin.

4-Methoxyphenyl- $\beta$ - $\beta$  dibromostyrene. -4-Hydroxybenzaldehyde (5g,  $3.67 \times 10^{-2}$  mol) was added to a solution of carbon tetrabromide (24.4g,  $7.35 \times 10^{-2}$  mol) and triphenylphosphine (38.5g,  $1.47 \times 10^{-1}$  mol) in dichloromethane (50ml), sealed under nitrogen and stirred for two hours at room temperature. The solution was poured into a large stirred volume of pentane, filtered, and reduced in volume to yield a white solid residue which was subjected to column chromatography on silica gel eluting with petroleum spirit/dichloromethane (70:30). The one major band eluted from the column was reduced in volume to yield the  $\beta$ , $\beta$ -dibromostyryl derivative **56** (6.9gm, 64%) as a white solid. MS (EI) found  $m/z = 292$ ,  $[M^+]$  requires  $m/z = 292$ .  $^1\text{H}$  nmr  $\delta$  (ppm,  $\text{CDCl}_3$ ) 7.526, 7.502, 6.908, 6.884 (AB spin quartet, 4H, phenyl-H,  $J_{AB} = 8.64$  Hz), 7.41 (s, 1H,  $\text{CH}=\text{CBr}_2$ ), 3.83 (s, 3H, terminal methyl group next to the oxygen).

4-Methoxyphenylpropynal- The  $\beta$ , $\beta$ -dibromostyryl derivative **56** (3.6g,  $1.23 \times 10^{-2}$  mol) was dissolved in dry THF (80-100ml), sealed under nitrogen and the reaction temperature lowered to  $-78^\circ\text{C}$  (cardice/acetone bath). BuLi (16.95ml,  $2.71 \times 10^{-2}$  mol) was added dropwise to the mixture and left to stir at  $-78^\circ\text{C}$  for one hour. DMF (1.9mls) was added and the mixture left to stir for a further hour at  $-78^\circ\text{C}$ . The reaction mixture was allowed to warm to room temperature and left for another hour. The mixture was poured into a stirred flask of iced water (600ml) acidified with concentrated hydrochloric acid (5ml). The pH of the solution was increased to pH 6-7 by the slow addition of a saturated solution of sodium carbonate, ensuring the pH did not rise above pH 8. The product was extracted with several portions of diethyl ether, dried over magnesium sulphate, filtered and reduced in volume to give a yellow/brown oil. The oily residue was subjected to column chromatography on silica gel eluting with petroleum spirit/dichloromethane (80:20). The main band eluted from the column was concentrated to yield the desired 4-methoxyphenylpropynal **57** (1.19g, 60%) as a yellow solid. MS (EI) found  $m/z = 160$ ,  $[M^+]$  requires  $m/z = 160$ .  $^1\text{H}$  nmr  $\delta$  (ppm,  $\text{CDCl}_3$ ), 9.40 (s, 1H,  $\text{CHO}$ ), 7.577, 7.554, 6.928, 6.905 (AB spin quartet, 4H, phenyl-H,  $J_{AB} = 8.28$  Hz), 3.85 (s, 1H,  $\text{OCH}_3$ ).

#### 4-Methoxyphenylethynyl dipyrromethane

The previous aldehyde **57** (0.54g,  $3.38 \times 10^{-3}$  mol) and pyrrole (11.3g,  $1.7 \times 10^{-1}$  mol) were degassed with nitrogen for ten minutes then the flask was sealed under nitrogen. The reaction temperature was lowered to  $-25^{\circ}\text{C}$  (cardice/carbon tetrachloride), a catalytic amount of  $\text{BF}_3 \cdot \text{OEt}_2$  (138 $\mu\text{l}$ ,  $1.13 \times 10^{-3}$  mol) was added to the mixture and allowed to stir for thirty minutes. Dichloromethane (50ml) was added to the mixture and then washed with two 50ml aliquots of 0.1M sodium hydroxide. The organic layer was then washed with several portions of water, dried over sodium sulphate, filtered and reduced in volume to give a brown oil. The oil was immediately subjected to column chromatography on silica gel eluting with cyclohexane/ ethylacetate/ triethylamine (65:34:1). The major band eluted from the column was reduced in volume to yield the desired dipyrromethane **58** (0.71g, 76%) as a brown solid. MS (EI); found  $m/z = 276$ ,  $[\text{M}^+]$  requires  $m/z = 276$ .  $^1\text{H}$  nmr  $\delta$  (ppm,  $\text{CDCl}_3$ ) 8.22 (br s, 2H, N-H), 7.412, 7.388, 6.855, 6.831 (AB spin quartet, 4H, phenyl-H,  $J_{\text{AB}} = 8.64$  Hz) 6.73, 6.71, 6.18, 6.16 (m, 6H, pyrrole  $\beta$ -H) 5.38 (s, 1H, methine bridge-H), 3.81 (s, 3H,  $\text{OCH}_3$ ).

4-Methoxyphenyl  $\text{Co}_2(\text{CO})_6$ -ethynyl-protected aldehyde<sup>(6)</sup> - Aldehyde **57** (1g,  $6.25 \times 10^{-3}$  mol) was added to a solution of  $\text{Co}_2(\text{CO})_8$  (2.14g,  $6.25 \times 10^{-3}$  mol) in dry THF (25ml) and left to stir under nitrogen, at room temperature until the effervescence of CO ceased. The reaction was stopped after thirty minutes and the excess solvent removed under vacuum to yield a brown solid residue which was subjected to column chromatography on silica gel eluting with dichloromethane/petroleum spirit (30:70). The major band eluted from the column was concentrated to yield the  $\text{Co}_2(\text{CO})_6$  protected aldehyde **59** (2.41g, 86%) as a chocolate brown solid. IR-loss of the characteristic ethynyl band at  $2196 \text{ cm}^{-1}$  and the appearance of terminal carbonyl groups centred around  $2062 \text{ cm}^{-1}$ .  $^1\text{H}$  nmr  $\delta$ (ppm,  $\text{CDCl}_3$ ), 10.52 (s, 1H,  $\text{CHO}$ ), 7.566, 7.543, 6.914, 6.891 (AB spin quartet, 4H, phenyl-H,  $J_{\text{AB}} = 8.28$  Hz), 3.84 (br s, 3H,  $\text{OCH}_3$ ).



5,10,15,20-meso-Tetra (Co<sub>2</sub>(CO)<sub>6</sub>-ethynyl-protected) porphyrin - Aldehyde 59 (1g, 2.24 x 10<sup>-3</sup> mol) and pyrrole (0.15g, 2.24 x 10<sup>-3</sup> mol) were dissolved in dry dichloromethane (190ml) and degassed with nitrogen for ten minutes. The reaction was sealed under nitrogen, the reaction temperature reduced to -25°C, shielded from the light and left for ten minutes. A catalytic amount of BF<sub>3</sub>.OEt<sub>2</sub> (92μl, 7.47 x 10<sup>-4</sup> mol) was added and the reaction left for twelve hours. DDQ (0.499g, 2.2 x 10<sup>-3</sup> mol) was added and the solvent removed under vacuum to yield a red/brown solid which was subjected to column chromatography on silica gel, eluting with dichloromethane/petroleum spirit (60:40). The major band and the first band eluted from the column was reduced in volume to yield the Co<sub>2</sub>(CO)<sub>6</sub> protected porphyrin 61 (0.42g, 43%) as a red/brown solid. (found: C, 44.78; H, 2.58; N, 2.58. C<sub>80</sub>N<sub>38</sub>N<sub>4</sub>O<sub>28</sub>Co<sub>8</sub>.9H<sub>2</sub>O requires C, 44.96; H, 2.64; N, 2.62%). UV/visible spectroscopy gives no clear indication of a porphyrin as the bands around 420, 500-650 nm were extremely broad and weak.

<sup>1</sup>H nmr δ(ppm, CDCl<sub>3</sub>) 9.00 (s, 8H, pyrrole β-H), 7.409, 7.385, 6.791, 6.767 (AB spin quartet, 16H, phenyl-H, J<sub>AB</sub> = 8.64 Hz), 3.82 (s, 12H, OCH<sub>3</sub>), -3.18 (br s, 2H, porphyrin N-H).

4-(1-Iododecyloxy) benzaldehyde - 4-Hydroxybenzaldehyde (3gm,

2.45 x 10<sup>-2</sup> mol), 1,10-diiododecane (38.8g, 9.83 x 10<sup>-2</sup> mol) and caesium carbonate (16g, 4.9 x 10<sup>-2</sup> mol) were brought to reflux in acetonitrile (100ml). The reaction was followed by TLC and stopped after three hours, the mixture filtered and the solvent removed under vacuum to yield a solid residue. The solid residue was subjected to column chromatography on silica gel, eluting with dichloromethane/petroleum spirit (40:60) to yield the desired product 62 (7.1gm, 75%) as a white solid. MS (EI). Found: m/z = 388, 261 [M<sup>+</sup>] requires m/z = 388. [M-I<sup>+</sup>] requires m/z = 261. <sup>1</sup>H nmr δ(ppm, CDCl<sub>3</sub>), 9.88 (s, 1H, CHO), 7.840, 7.817, 7.004, 6.981 (AB spin quartet, 4H, aromatic phenyl-H, J<sub>AB</sub> = 8.28 Hz), 4.06, 4.04, 4.02 (t, 2H, OCH<sub>2</sub>CH<sub>2</sub>), 3.21, 3.19, 3.17 (t, 2H, CH<sub>2</sub>CH<sub>2</sub>I), 1.85-1.77 (m, 4H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, CH<sub>2</sub>CH<sub>2</sub>I),

1.32 (complex s, 12H, [CH<sub>2</sub>]<sub>6</sub>).

4-(1-Iododecyloxyphenyl)-dibromostyrene - To a stirred solution of carbon tetrabromide (10.95g,  $3.30 \times 10^{-2}$  mol) in dry dichloromethane (150ml) at 0°C, triphenylphosphine (17.28g,  $6.60 \times 10^{-2}$  mol) was added, and the clear solution turned yellow/orange with vigorous effervescence. When the effervescence had ceased, aldehyde **62** (6.4g,  $1.65 \times 10^{-2}$  mol) was added slowly and the reaction temperature brought to room temperature. The reaction vessel was sealed under nitrogen and left to stir for several hours. On completion, the mixture was poured into a stirred volume of petroleum spirit (600ml), stirred, left to settle and filtered to remove the precipitate. The solvent was reduced in volume and the resulting residue was subjected to column chromatography on silica gel eluting with petroleum spirit/dichloromethane (60:40) to yield the desired  $\beta,\beta$ -dibromostyryl derivative **63** (7.14g, 80%) as a white solid. MS (EI) - found  $m/z = 544, 418$ , [M<sup>+</sup>] requires  $m/z = 544$ , [M-I<sup>+</sup>] requires  $m/z = 418$ . <sup>1</sup>H nmr  $\delta$ (ppm, CDCl<sub>3</sub>), 7.508, 7.484, 6.886, 6.862 (AB spin quartet, 4H, aromatic phenyl-H,  $J_{AB} = 8.64$  Hz), 7.40 (s, 1H, CH=CBr<sub>2</sub>), 3.98, 3.96, 3.94 (t, 2H, OCH<sub>2</sub>CH<sub>2</sub>), 3.43, 3.41, 3.39 (t, 2H, CH<sub>2</sub>CH<sub>2</sub>I), 1.87-1.75 (m, 4H, two OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>I), 1.31 (complex s, 12H, [CH<sub>2</sub>]<sub>6</sub>).

4-(1-Iodo-decyloxy-4-phenylpropynal - The previous  $\beta,\beta$ -dibromostyryl derivative **63** (6.2g,  $1.14 \times 10^{-2}$  mol) was dissolved in dry tetrahydrofuran (150ml), sealed under nitrogen and the reaction temperature lowered to -78°C (cardice/acetone bath). BuLi (17.8ml,  $2.85 \times 10^{-2}$  mol) was added dropwise to the solution and the mixture was stirred at -78°C for one hour. Dimethylformamide (1.78ml) was added and the mixture stirred at -78°C for a further hour. The reaction mixture was warmed to room temperature and left for another hour, then poured into a stirred volume of iced water (600ml), acidified with concentrated hydrochloric acid (6ml). The pH of the mixture was increased to pH 6-7 by the slow addition of a saturated solution of sodium carbonate, ensuring the pH did not rise above pH 8. The product was extracted with several portions of diethyl ether, dried over magnesium sulphate,

filtered and reduced in volume to give a yellow/ brown oil. The oily residue was subjected to column chromatography on silica gel eluting with petroleum spirit/dichloromethane (80:20) to yield the desired acetylene aldehyde **64** (3.02g, 65%) as a yellow solid. MS (EI) - found  $m/z = 412, 286$ ,  $[M]^+$  requires  $m/z = 412$ ,  $[M-I]^+$  requires  $m/z = 286$ .  $^1\text{H}$  nmr  $\delta$  (ppm,  $\text{CDCl}_3$ ), 9.39 (s, 1H,  $\text{CHO}$ ), 7.561, 6.537, 6.909, 6.885, (AB spin quartet, 4H, aromatic phenyl-H,  $J_{AB} = 8.64$  Hz), 4.01, 3.99, 3.97 (t, 2H,  $\text{OCH}_2\text{CH}_2$ ), 3.43, 3.41, 3.39, (t, 2H,  $\text{CH}_2\text{CH}_2\text{I}$ ), 1.87-1.77 (m, 4H, two  $\text{OCH}_2\text{CH}_2\text{CH}_2$ ,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{I}$ ), 1.31 (complex s, 12H,  $[\text{CH}_2]_6$ ).

4-(1-Iododecyloxy) phenylethynyl dipyrromethane -pyrrole (1.6g,  $2.39 \times 10^{-2}$  mol) and the previously synthesised aldehyde **64** (0.2g,  $4.85 \times 10^{-4}$  mol) were degassed with nitrogen for ten minutes, sealed under nitrogen and the reaction temperature lowered to  $-25^\circ\text{C}$  (cardice/carbontetrachloride bath). A catalytic amount of  $\text{BF}_3 \cdot \text{OEt}_2$  (20  $\mu\text{l}$ ,  $1.6 \times 10^{-4}$  mol) was added and the reaction mixture stirred for thirty minutes. Dichloromethane (50ml) was added to the mixture and then washed with two portions of sodium hydroxide (50ml, 0.1M). The organic layer was then washed several times with water, dried over sodium sulphate, filtered and reduced in volume to give a brown oily residue. This was immediately subjected to column chromatography on silica gel, eluting with petroleum spirit/ethyl acetate/triethylamine (80:19:1). The major band to be eluted was concentrated to give the desired product **65** (0.21g, 82%) as a brown solid. MS (EI) - found  $m/z = 528$ ,  $[M]^+$  requires  $m/z = 528$ .

$^1\text{H}$  nmr  $\delta$ (ppm,  $\text{CDCl}_3$ ).8.22 (br s, 2H, N-H), 7.396, 7.372, 6.839, 6.815 (AB spin quartet, 4H, aromatic phenyl-H,  $J_{AB} = 8.64$  Hz ), 6.73, 6.72, 6.17 (m, 6H, pyrrole  $\beta$ -H), 5.38 (s, 1H, methine bridge-H), 3.97, 3.95, 3.93 (t, 2H,  $\text{OCH}_2\text{CH}_2$ ), 3.43, 3.41, 3.39 (t, 2H,  $\text{CH}_2\text{CH}_2\text{I}$ ), 1.89-1.74 (m, 4H, two  $\text{OCH}_2\text{CH}_2\text{CH}_2$ ,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{I}$ ), 1.31 (complex s, 12H  $[\text{CH}_2]_6$ ).

5,10,15,20-meso-Tetra-(4-(1-iododecyloxyphenyl ethynyl) porphyrin -

Borontrifluoride dietherate (16 $\mu$ l,  $1.26 \times 10^{-4}$  mol) was added to a stirred, nitrogen degassed solution of 4-(1-iododecyloxy)phenylpropynal (0.16g,  $3.78 \times 10^{-4}$  mol) and 4-(1-iododecyloxy) phenylethyndipyrromethane (0.2g,  $3.78 \times 10^{-4}$  mol) in dry, distilled dichloromethane (40ml) at  $-25^{\circ}\text{C}$ . The reaction mixture was kept at this temperature for three hours, then allowed to warm to room temperature overnight. DDQ (0.086g,  $3.78 \times 10^{-4}$  mol) was added and the solvent removed under vacuum to give a green/black solid residue. The solid residue was subjected to column chromatography on silica gel, eluting with dichloromethane to yield a green sticky solid which was triturated with methanol to yield the 5,10,15,20-meso-tetra-(4-(1-iododecyloxy) phenylethyndipyrromethane) porphyrin 66 (0.041g, 12%) as a green powder. m.pt.  $138-140^{\circ}\text{C}$ , (found C, 62.23; H, 6.70; N, 2.73,  $\text{C}_{92}\text{H}_{106}\text{N}_4\text{O}_4\text{I}_4 \cdot 2\text{C}_6\text{H}_{14}$ ; requires C, 62.08; H, 6.71; N, 2.78%). FABS-MS (3-NOBA,  $\text{CHCl}_3$ ); found  $m/z = 1839$ .  $[\text{M}^+]$  requires  $m/z = 1839$ .  $\lambda_{\text{max}}$  nm ( $\epsilon \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ ,  $\text{CHCl}_3$ ) 472 (278000), 655 (87000), 745 (55000).  $^1\text{H}$  nmr  $\delta$  (ppm,  $\text{CDCl}_3$ ), 9.18 (s, 8H, pyrrole  $\beta$ -H), 7.920, 7.897, 7.067, 7.044 (AB spin quartet, 16H, aromatic phenyl-H,  $J_{\text{AB}} = 8.28$  Hz), 4.10, 4.08, 4.06 (t, 8H,  $\text{OCH}_2\text{CH}_2$ ), 3.47, 3.45, 3.43 (t, 8H,  $\text{CH}_2\text{CH}_2\text{I}$ ), 1.91-1.88 (m, 16H,  $\text{OCH}_2\text{CH}_2\text{CH}_2$ ,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{I}$ ) 1.38 (complex s, 48H,  $[\text{CH}_2]_6$ ), -2.75 (br s, 2H, porphyrin N-H).

5,10,15,20-meso-Tetra-(4-(1-iododecyloxy)phenylethyndipyrromethane) porphyrinato-zinc -

The previous porphyrin (0.022 g,  $1.195 \times 10^{-5}$  mol) was dissolved in chloroform and heated to  $50^{\circ}\text{C}$  on a water bath. A saturated solution of zinc acetate in methanol was added and the reaction followed by UV/visible spectroscopy. The reaction was stopped and the solvent removed under pressure. The solid residue was dissolved in methanol to remove any zinc acetate, and filtered. The solid residue was then extracted with dichloromethane and reduced in volume to give a green solid which was subjected to column chromatography on silica gel eluting with dichloromethane/petroleum spirit (50:50) to yield the desired 5,10,15,20-mesotetra-(4-(1-iododecyloxy)phenylethyndipyrromethane)porphyrinato zinc 67 (0.019g,

84%) as a green solid. m.pt. = 150-153°C. (found C, 64.85; H, 6.32; N, 3.00,  $C_{92}H_{104}N_4O_4I_4.Zn.2C_6H_{14}$  requires C, 60.19; H, 6.41; N, 2.70%). FABS-MS (3-NOBA,  $CDCl_3$ ) found:  $m/z = 1903$ ,  $[M]^+$  requires  $m/z = 1903$ .  $\lambda_{max}$  nm ( $\epsilon \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ ,  $CHCl_3$ ) 482 (240000), 636 (15000), 692 (40000).  $^1H$  nmr  $\delta$ (ppm,  $CDCl_3$ ), 8.62 (s, 8H, pyrrole  $\beta$ -H), 7.709, 7.688, 6.884, 6.863 (AB spin quartet, 16H, aromatic phenyl-H,  $J_{AB} = 7.56 \text{ Hz}$ ), 3.97, 3.95, 3.93 (t, 8H,  $OCH_2CH_2$ ) 3.42, 3.40, 3.39 (t, 8H,  $CH_2CH_2I$ ) 1.94-1.85(m, 16H,  $OCH_2CH_2CH_2$ ,  $CH_2CH_2CH_2I$ ), 1.40 (complex s, 48H,  $[CH_2]_6$ ).

4-Nitrophenylethynyldiethylacetal<sup>(7)</sup> - A mixture of 4-iodonitrobenzene (1g, 4 mmol), triphenylphosphine palladium chloride (0.062g, 0.088 mmol), copper iodide (0.012g, 0.064 mmol) were dissolved in dry triethylamine (10ml) and degassed with nitrogen for ten minutes. To the mixture, propionaldehyde diethylacetal (0.61g, 4.8 mmol) was added, sealed under nitrogen and allowed to stir for five minutes. A brown solid precipitated out which was extracted from water with diethyl ether. The water layer was washed several times with diethyl ether, the extracts combined, were dried over magnesium sulphate, filtered and reduced in volume to give a brown oil. The oily residue was subjected to column chromatography on silica eluting with petroleum spirit/ethyl acetate (5:1) to yield a yellow oil **69** (0.87g, 87%). MS (EI) - found  $m/z = 249$ ,  $[M^+]$  requires  $m/z = 249$ .  $^1H$  nmr  $\delta$ (ppm,  $CDCl_3$ ) = 8.205, 8.181, 7.640, 7.616 (AB spin quartet, 4H, aromatic phenyl H,  $J_{AB} = 8.64 \text{ Hz}$ ), 5.51 (s, 1H, CH proton next to the ethynyl group), 3.84, 3.82, 3.81, 3.80 (q, 2H,  $OCH_2CH_3$ ), 3.70, 3.68, 3.67, 3.66 (q, 2H,  $OCH_2CH_3$ ), 1.31, 1.29, 1.27 (t, 6H,  $CH_2CH_3$ ).

4-Nitrophenylpropynal<sup>(6)</sup> - To a mixture of concentrated sulphuric acid (1gm), and water (2ml), DMSO (4ml) and the previous diacetal (0.58g,  $2.5 \times 10^{-3}$  mol) were added, the reaction temperature increased to 95°C and left for thirty minutes. The reaction was stopped and added to a saturated solution of ammonium chloride. The product was extracted several times with diethyl ether, dried over magnesium sulphate, filtered and reduced in volume to give a yellow-brown oil. The oily residue was subjected to column chromatography

on silica gel, eluting with dichloromethane/petroleum spirit (80:20) to yield the 4-nitrophenylpropynal **70** (0.21g, 51%) as a yellow solid. MS (EI) - found  $m/z$  = 175,  $[M^+]$  requires  $m/z$  = 175.  $^1\text{H}$  nmr  $\delta$ (ppm,  $\text{CDCl}_3$ ) 9.46 (s, 1H, CHO), 8.294, 8.270, 7.785, 7.761 (AB spin quartet, 4H, aromatic Phenyl -H,  $J_{AB}$  = 8.64 Hz). Infrared confirms the characteristic stretches at  $2194\text{ cm}^{-1}$  for the acetylenic bond and  $1518, 1344\text{ cm}^{-1}$  for the  $\text{NO}_2$  bond.

5,10,15-Tris(4-dodecyloxyphenylethynyl)-20-(4-nitrophenylethynyl) porphyrin - 4-dodecyloxyphenylethynyldipyrromethane **46** ( $0.3\text{g}, 6.97 \times 10^{-4}\text{ mol}$ ) and 4-nitrophenylpropynal **70** ( $0.122\text{g}, 6.97 \times 10^{-4}\text{ mol}$ ) were dissolved in dry dichloromethane (50ml) and degassed with nitrogen. The reaction vessel was sealed under nitrogen and the reaction temperature reduced to  $-25^\circ\text{C}$ . A catalytic amount of boron trifluoride diethyletherate ( $29\mu\text{l}, 2.32 \times 10^{-4}\text{ mol}$ ) was added and the reaction mixture was left at  $-25^\circ\text{C}$  for three hours. The mixture was warmed to room temperature and left overnight. DDQ ( $0.122\text{g}, 5.3 \times 10^{-4}\text{ mol}$ ) was added and the solvent removed under pressure to give a black/green solid. The solid residue was subjected to column chromatography on silica gel, eluting with dichloromethane/petroleum spirit (60:40). The main band eluted from the column was concentrated, triturated with methanol and filtered to yield 5,10,15-tris-(4-dodecyloxyphenylethynyl)-20-(4-nitrophenylethynyl) porphyrin **71** ( $0.045\text{g}, 11\%$ ) as a green solid. m.pt.  $115-118^\circ\text{C}$ . (found: C, 79.80; H, 7.85; N, 5.00,  $\text{C}_{88}\text{H}_{101}\text{N}_5\text{O}_5 \cdot \text{CH}_3\text{OH}$  requires C, 79.72; H, 7.89; N, 5.22%).  $\lambda_{\text{max}}$  nm ( $\epsilon\text{ mol}^{-1}\text{ dm}^3\text{ cm}^{-1}$ ,  $\text{CHCl}_3$ ) 478 (255000), 648 (76000), 741 (40000). FABS-MS (3NOBA,  $\text{CH}_2\text{Cl}_2$ ) found  $m/z$  = 1309, 1263, 880,  $[M^+]$  requires  $m/z$  = 1309,  $[M-\text{NO}_2]$  requires  $m/z$  = 1263,  $[M-\text{dodecylphenylethynyl}-(4\text{nitrophenyl})]$  requires  $m/z$  = 880.

$^1\text{H}$  nmr  $\delta$  (ppm  $\text{CDCl}_3$ ) 8.406, 8.395, 8.258, 8.247 (AB spin quartet, 4H,  $\beta$ -pyrrolic -H,  $J_{AB}$  = 3.96 Hz), 7.863, 7.840, 7.235, 7.213 (AB spin quartet, 4H, aromatic phenyl H,  $J_{AB}$  = 7.92 Hz), 7.624, 7.613, 7.131, 7.126 (AB spin quartet, 4H,  $\beta$ -pyrrolic-H,  $J_{AB}$  = 3.96 Hz), 7.533, 7.511, 6.890, 6.869 (AB spin quartet, 4H, aromatic phenyl-H,  $J_{AB}$  = 7.92 Hz), 7.461, 7.440, 6.788, 6.767

(AB spin quartet, 8H, aromatic phenyl H,  $J_{AB} = 7.56$  Hz) 4.04 (m, 2H,  $\text{OCH}_2\text{CH}_2$ ), 3.98, 3.96, 3.94 (t, 4H,  $\text{OCH}_2\text{CH}_2$ ), 1.94-1.90 (m, 6H,  $\text{OCH}_2\text{CH}_2\text{CH}_2$ ), 1.60-1.47 (m, 6H,  $\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.38 (complex s, 32H,  $[\text{CH}_2]_8$ ), 1.25 (complex s, 16H,  $[\text{CH}_2]_8$ ) 0.98, 0.97, 0.95 (t, 9H,  $\text{CH}_2\text{CH}_3$ ), -6.35 (br s, 2H porphyrin N-H).

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