The Synthesis and Characterisation of Phthalocyanines with Dendritic Substituents

A thesis submitted to the University of Manchester for the degree of Doctor of Philosophy in the Faculty of Science

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September 1997

Contents

Abstract

The aim of this project was to synthesise, characterise and examine the relevant properties of a number of novel substituted phthalocyanine (Pc) derivatives, with particular reference to the preparation and substitution of dendritic fragments. Substitution of the dendrimer moieties was achieved both peripherally and axially in an attempt to alleviate the extent of Pc aggregation in both the solid and solution phase and to synthesise both anisotropic structured glassy solids and isotropic glasses.

The synthesis of the dendrimer fragments was achieved initially by using the *convergent* approach to dendrimer synthesis. However, this method proved to be very time consuming and only produced lower generation dendrimers in poor yield, so alternative methods of dendrimer synthesis were employed.

Phthalonitrile precursors containing one and two dendritic wedges were successfully synthesised for the dendrimers produced. However the cyclotetramerisation reactions of the dendritically substituted phthalonitriles to produce the analogous Pcs only produced poor yield of low generation dendrimers, probably due to steric constraints of the dendrimers around the final macrocycle.

Therefore, to try to alleviate this problem, phthalonitriles were synthesised with flexible spacers between the dendrimer and what will become the periphery of the macrocycle, and also phthalonitriles with dendrimers based on different initial monomer units. Yields of Pcs were slightly improved in these cases.

Unsymmetrical Pcs were also prepared by the cyclotetramerisation of two different phthalonitrile precursors. The mixture of Pcs was then easily separated due to the difference in polarity of the resultant Pc molecules. Hence, any steric problems were completely avoided and anisotropic structured glassy solids synthesised.

Axially substituted Pcs based on $SiPcCl_2$ were synthesised and as expected were isotropic glasses. The series of Pcs showed a decrease in aggregation as the bulky dendritic substituent grows larger. The spectrochemical properties of all Pcs synthesised are discussed.

The material properties of the Pcs were also investigated. Most peripheral derivatives exhibited discotic liquid crystalline behaviour and the mesophases were examined by Differential Scanning Calorimetry, Optical Microscopy and in the case of the unsymmetrical Pc series, by X-ray Diffraction.

Declaration

No portion of the work referred to in this thesis has been submitted in support of an application for another degree or qualification of this or any other university or other institute of learning.

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The Author

The Author graduated from Manchester University in 1993 with a BSc. (Hons) degree in Chemistry with Polymer Science placed in the first class. Before going to university, she had worked within the Strategic Polymer Research Group at Courtaulds Research Coventry and is currently working for Kodak Ltd. as a management trainee.

Acknowledgement

I would like to thank my Supervisor Dr. N. B. McKeown for his helpful and informative discussions on both a professional and personal level, during my years of working with him .

My special thanks must also go to Dr. Guy Clarkson, without whom Mc. Slap would never have been invented, the joys of 'Summer of 69' never discovered and this 'That's Research Wee Man' project NEVER completed!! I owe it all to you Guy!

I must also thank all members past and present, of the organic and physical polymer research groups (incase I forget to mention anyone personally!) and my friends from other sections who made my time in Manchester memorable and character building!! Especially Drs. Paul Humberstone (right from the hockey days until the present day!), Jeremy (Jez) Ward and Martin (sticks a mean pair of tweezers in the ceiling) Woolley, for their continual and amusing anecdotes making the early days in the lab fun. Thanks also to my 'old mate from Undergraduate days' Matt Brewis, for being a revision partner, travelling companion and fellow dendrimer synthesiser (so he can appreciate the frustration!) for all these years, but most of all for being a good friend.

Thanks also to the original lab members, Naz, Pete, Chris and of course The Baron, I still think of you all! and to Clare and Penny for making my final year less stressful! Finally from the lab members I must thank 'Uncle Mick' Rabjohns for making me part of his 'big happy polymer family', El Neilo Thompson for being a complete Nutter and H, especially H,

without whom I wouldn't have survived last summer, BeerHenge IV and birthday burgers!! Long may they continue!!

I would like to thank my living companions during my Ph.D., Mark (Cat) Peterson and Paul (Tommy) Thompson. I did enjoy cleaning up after you boys!! But didn't we have a great time! and of course, Sean, for always being there for me (when he wasn't in Jabez!) and being my tower of support and strength the whole time.

My special thanks must also go to Nicki, for being my 'best girlie friend' during my Ph.D. and for persuading me to apply for a job a Kodak because she missed me so much!

I must express my sincere thanks to my Mum and Dad who have always supported me both financially and emotionally in whatever I have decided to do and to Richard and Andie for doing what only Big brothers and their Girlfriends can do!

And very finally my last thanks and love go to Victor, who might not have been there during the Manchester part, but has stopped my world from falling apart around me during the write up.

List of Abbreviations used in this Thesis

[G-1]-OH *3, 5-dibenzyloxybenzyl alcohol*

[G-1]-Br *3, 5-dibenzyloxybenzyl bromide*

[G-2]-OH *(3, 5-di(3', 5'-dibenzyloxy)benzyloxy)benzyl alcohol*

[G-2]-Br *(3, 5-di(3', 5'-dibenzyloxy)benzyloxy)benzyl bromide*

[G-3]-OH *(3, 5-di(3', 5'-di(3'', 5''-dibenzyloxy)benzyloxy)benzyloxy)benzyl alcohol*

DCM *Dichloromethane*

THF *Tetrahydrofuran*

EtOAc *Ethyl Acetate*

MeOH *Methanol*

NaOH *1M Sodium Hydroxide*

DMF *Dimethyl Formamide*

DCCI *Dicyclohexylcarbodiimide*

$LiAlH_4$ *Lithium Aluminium Hydride*

For my Nana, even though I know you wouldn't have understood this, you made sure you knew what phthalocyanines are and you would have been so proud of me.

1

Introduction

1.1 An Introduction to the Phthalocyanines

1.1.1 Discovery and Determination of Structure

The first observation of the compound which later became known as phthalocyanine was during the preparation of *ortho*-cyanobenzamide from phthalamide and acetic acid.[1] Braun and Tcherniac, working at the South Metropolitan gas Company (London) in 1907, observed a dark insoluble material. Similarly in 1927, an attempt to prepare phthalonitrile from the reaction of *ortho*-dibromobenzene with copper cyanide in refluxing pyridine[2] by de Diesback and von der Weid of Freibourg University, resulted in a 23 % yield of a blue, insoluble, exceptionally stable material. The two by-products are now known to be metal-free (Fig 1.2a) and copper containing phthalocyanine respectively (Fig. 1.2b).

A year later at the Grangemouth factory of Scottish Dyes the full potential of the discovery of these two compounds was realised during the industrial preparation of phthalimide from phthalic anhydride. The glass lined vessel cracked which exposed the outer steel casing to the reaction and resulted in the formation of a blue-green impurity. Dissatisfaction with the purity of the product prompted investigation of the impurity and it was revealed that the iron containing by-product had potential as an exceptionally stable and insoluble pigment. A patent[3] covering the discovery and properties of the substance was filed the same year and described the preparation of what was later recognised as iron (II) tetrabenzotetraazaporphyrin (phthalocyanine) (Fig. 1.2c). The actual structure of phthalocyanine was later determined through the work of

Linstead[4, 5, 6, 7, 8] and the X-ray diffraction analyses of Robertson,[9, 10, 11] while examining both metal containing and metal-free phthalocyanines.

Linstead used a combination of elemental analyses, ebullioscopic molecular mass determination and oxidative degradation to arrive at the correct structure of H_2Pc and its simple metal derivatives. This determined that the structure of Pc is closely related to the naturally occurring porphyrin ring system, but with the difference being the four benzo subunits and the nitrogen atoms at each of the four *meso* positions. Pc is also referred to as tetrabenzotetraazaporphyrin and similarly displays aromatic stability due to the conjugated array of 18 π electrons, as predicted by Hückel's theory of aromaticity. Linstead coined the name *phthalocyanine* as a combination of the prefix *phthal* from the Greek *naptha* meaning rock oil, to emphasise the association with its various phthalic acid derived precursors and the Greek *cyanine* meaning blue.

Pcs are generally blue or green when in their normal oxidation state, show intense colouration in the solid and usually have a characteristic purple sheen when crystalline. X-ray studies on the structure of Pcs have generally shown a square planar arrangement of the Pc unit about a central metal atom. Virtually all metallic elements and a few non-metallic elements will form Pcs and the formation of the square planar species also provides two axial sites where additional chemistry can occur. This is discussed in section 2.8.2.

1.1.2 Uses and Applications of Phthalocyanines

Pcs have been used extensively as green and blue colourants for paints, textiles, plastics and metal surfaces. They are also especially well suited to the production of inks due to their intense colour and consequently most blue ballpoint pen ink is Pc based.

The Pc macrocycle also has fascinating electronic and optical properties which are of considerable interest. In recent years the synthesis of numerous Pc derivatives have been prepared to facilitate the exploitation of these properties in gas sensors, electrophotography, fuel cells, solar energy conversion, non-linear optics, catalysts and for photodynamic therapy in the treatment of cancer (PDT).[12]

There has been a considerable effort to produce materials in which the orientation and self-association of the Pc ring can be controlled. This includes the development of derivatives which possess liquid crystallinity (thermotropic or lyotropic)[13] or that are capable of forming well ordered Langmuir (LB) multi-layer films.[14] Pcs that are designed to be compatible with both methods of material fabrication are of particular interest.[15]

1.1.3 Electronic Properties

The history of metal containing Pcs began with their remarkable spectral properties.[16] The purity and depth of the colour of the simple metal Pc dyes with D_4h symmetry, (i.e. the metal ion lies in the plane of the Pc) arise from their unique property of having an isolated intense single band

located in the far red end of the spectrum near 670 nm called the Q-band and a much less intense band, lying just to the blue of the visible region near 340 nm called the B or Soret band. The main difference between simple metal Pcs and metal-free Pc is that the symmetry is lowered from D_4h to D_2h in the metal-free, thus causing a distinct splitting of the single band in the Q-band region of the absorption spectra (Fig. 1.1).

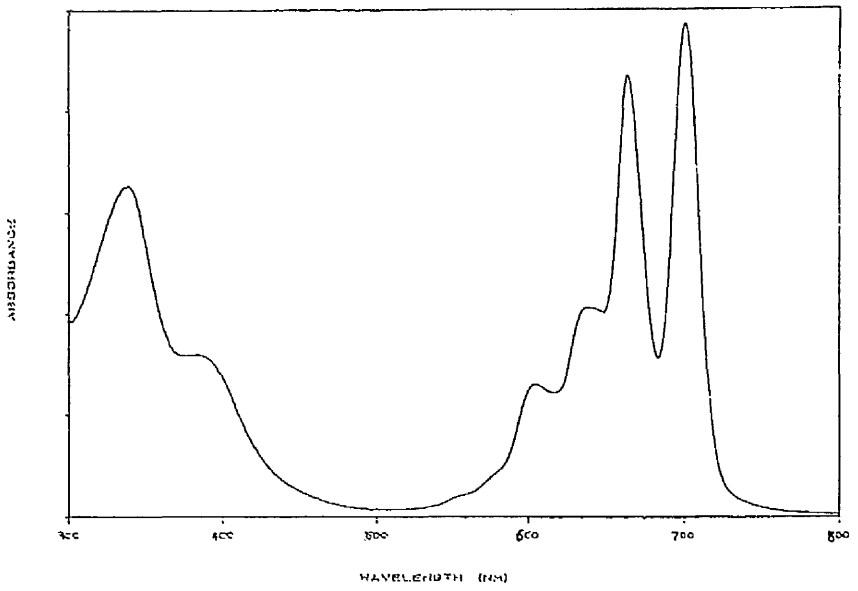
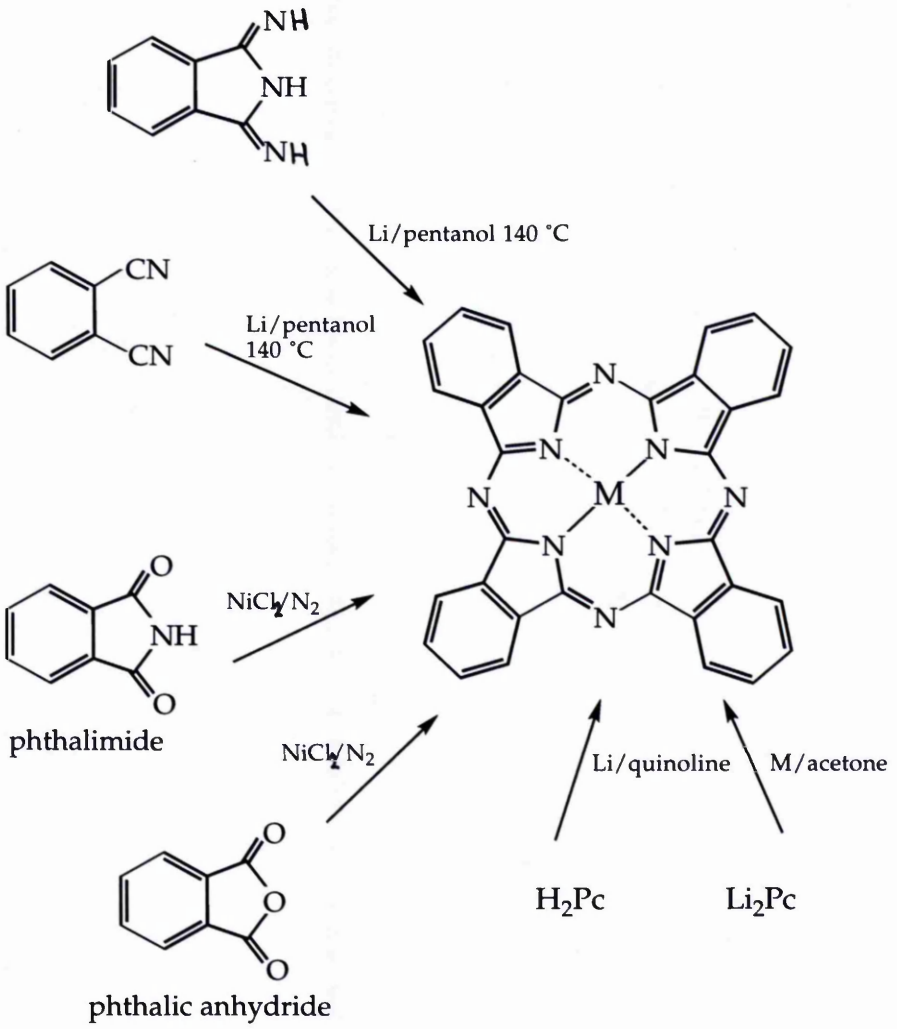


Fig. 1.1 Typical Visible Spectrum of a Metal-Free Pc.

1.1.4 Synthesis of Metallated Phthalocyanines (MPcs)

Whilst Linstead was carrying out his early work, it was discovered that Pcs could easily be prepared from a number of amide and nitrile derivatives of phthalic acid, by fusion with metals, metallic salts, oxides and sulphides.[4]

Most simple MPcs are prepared directly from the phthalonitrile or diiminoisoindoline using the metal ion as a template for the cyclotetramerisation (Scheme 1.1). Phthalic anhydride or phthalamide may additionally be used as precursors in the presence of a metal salt (e.g. copper acetate or nickel chloride etc) and a source of nitrogen (e.g. urea).



Scheme 1.1

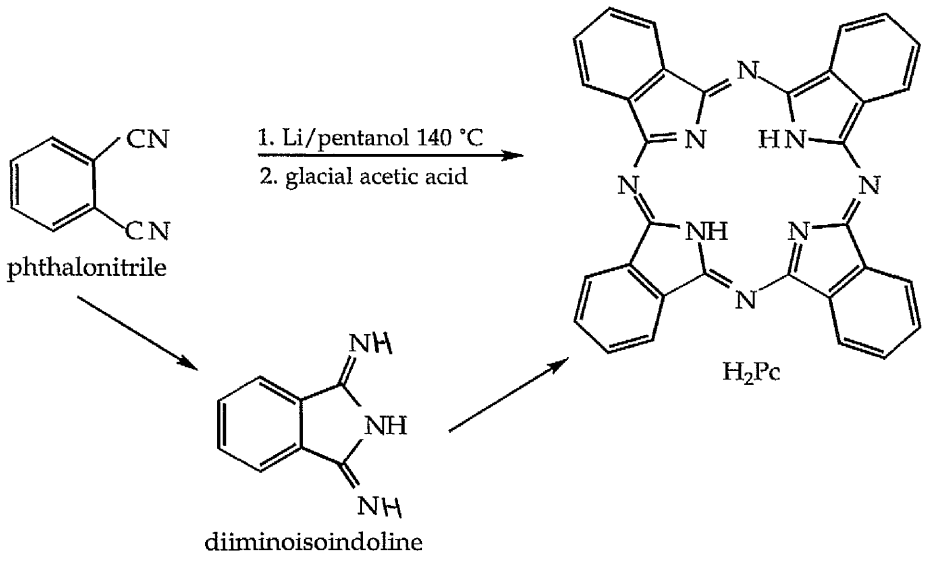
Alternatively, the reaction between H_2Pc or Li_2Pc and the appropriate metal salt produces most MPcs. However, a problem arises due to the insolubility of H_2Pc in most organic solvents. To overcome this a high

boiling aromatic solvent such as chloronapthalene or quinoline is required in order to ensure complete metallation.

The use of Li_2Pc as a precursor is easier due to the increased solubility of this complex in acetone or ethanol and the insoluble MPc precipitate is readily collected on completion of the metallation reaction.

1.1.5 Synthesis of Unsubstituted Metal-free Phthalocyanine (H_2Pc)

A number of ortho-disubstituted benzene derivatives can act as precursors in the synthesis of Pcs. In most cases the synthetic route proceeds through phthalonitrile (1,2 dicyanobenzene, Scheme 1.2) as an intermediate.

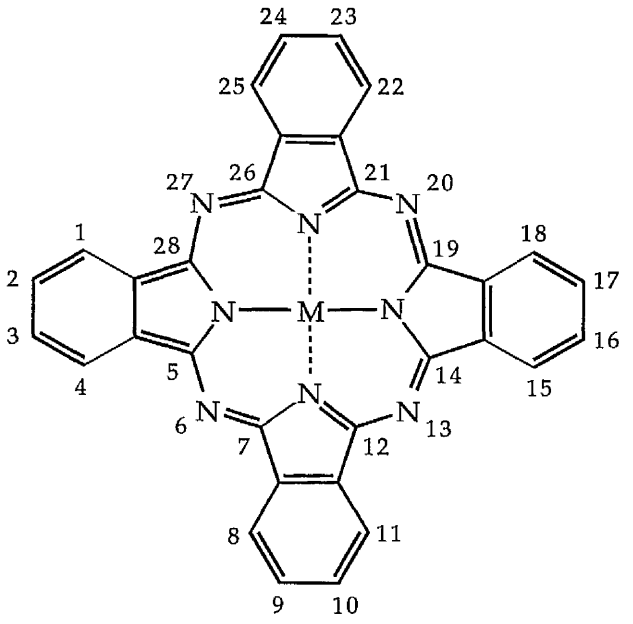


Scheme 1.2

There are several synthetic methods which can be used to affect cyclotetramerisation of phthalonitrile to form H_2Pc, although the full mechanisms are not known. These include the formation of diiminoisoindoline by the reaction of phthalonitrile with ammonia which can then condense under relatively mild conditions to form H_2Pc. Cyclotetramerisation of phthalonitrile in a melt with hydroquinone (4 : 1 by weight) as the reducing agent, allows H_2Pc preparation without the use of metal ions which may be incorporated into the material as impurities. H_2Pc can also conveniently be prepared from phthalonitrile using a refluxing solution of lithium metal or hydride (lithium pentyloxide) dissolved in pentanol to form Li_2Pc, which can be readily demetallated using dilute aqueous acid (Scheme 1.2).

1.1.6 Peripherally Substituted Phthalocyanines

Substituted phthalonitriles can be prepared from 1,2-dibromobenzenes by reaction with copper(I)cyanide, this allows a large number of Pc derivatives to be prepared. Within the last 20 years, Pcs have been synthesised which are substituted at the benzo unit with various side groups such as aliphatic and aromatic moieties, with linking groups such as ethers, esters and thioethers.[12] There are usually four or eight side groups per Pc ring (one or two per benzo unit producing a symmetrical substitution pattern), but other substitutions are possible up to a maximum of sixteen. The substitution pattern can be described as peripheral (occupying the 2, 3, 9, \0, \6, \7, 23 and 24 positions) or non-peripheral (1, 4, 8, 11, 15, 18, 22 and 25 positions), (Fig. 1.2).



1.1a M = Fe

1.1b M = Cu

1.1c M = H_2

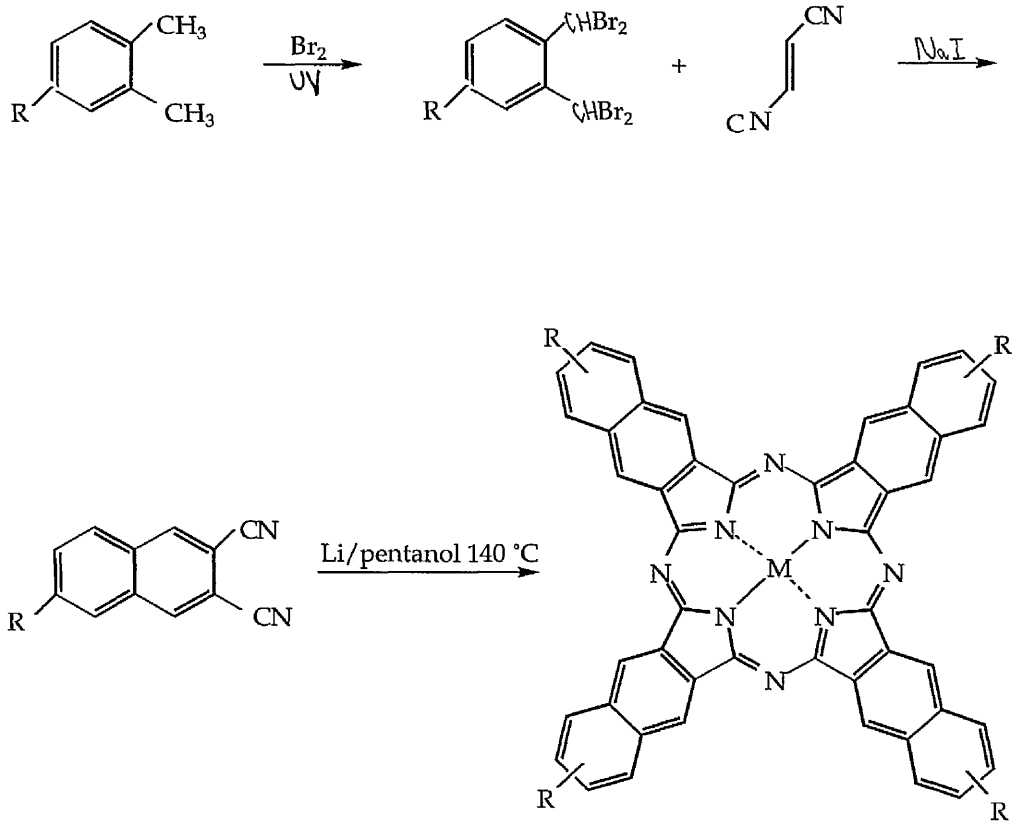
Fig. 1.2 Basic structure of an unsubstituted phthalocyanine (Pc).
(N.B. See Leznoff *et al* **12** for nomenclature of Pc system).

It must be noted that, in the absence of a line of symmetry bisecting the benzo unit (such as in the case of tetra substituted Pcs), four regioisomers are possible 2, 9, 16, 23- 2, 10, 16, 24- 2, 9, 17, 24- and 2, 9, 16, 24- Such Pcs are usually obtained in a statistically predictable mixture of these isomers and their properties are affected by this factor (e.g. crystallisation is suppressed, melting point lowered and solubility improved).

1.1.7 Naphthalocyanines (NPcs)

NPcs possess extended conjugated structures and absorb light in the near infra red (800 nm) even in solution. They are of interest as photoelectronic materials. A common synthetic route to NPcs, originally devised by Luk 'yanets and co-workers**17** is shown in Scheme 1.3. A number of

peripherally substituted derivatives with increased solubility are accessible by adapting this synthetic scheme.



Scheme 1.3

1.1.8 Unsymmetrically Substituted Phthalocyanines

Non-uniformly substituted Pcs have applications in oligomer or polymer synthesis and Langmuir Blodgett (LB) film fabrication. The most common route to unsymmetrical Pcs involves a mixed phthalonitrile or diiminoisoindoline cyclotetramerisation.[18] In theory for two different phthalonitriles there are six possible products (Fig 1.3).[19]

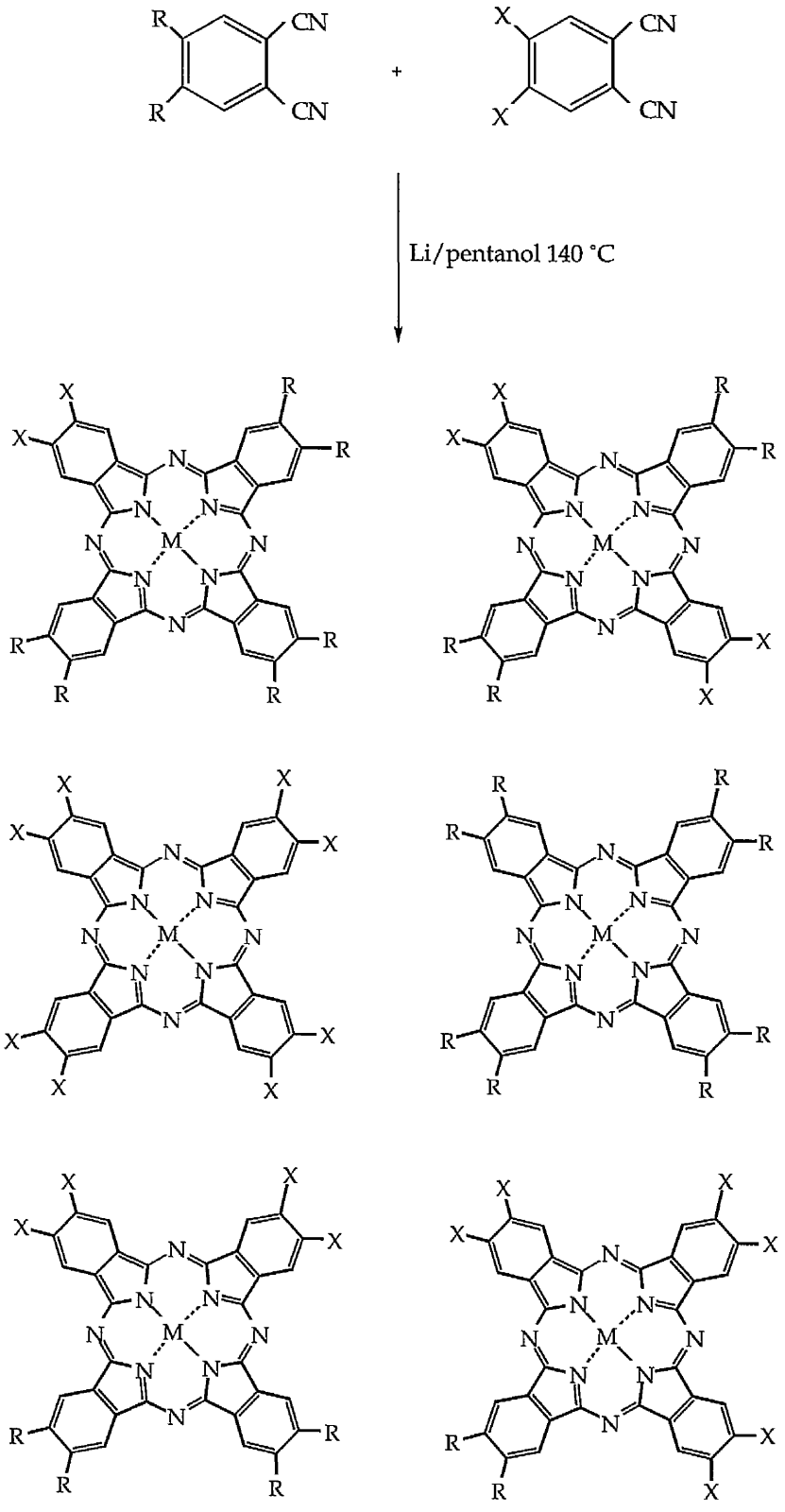


Fig. 1.3

To some extent a reasonable yield of the desired unsymmetrical Pc can be achieved by controlling the relative amount of the two precursors. However, in practice, mixed phthalonitrile reactions always yield significant quantities of at least two Pcs that need careful separation by chromatography. Therefore, the two different types of substituent (X and R in Fig. 1.3) need to be chosen so that the resultant soluble Pcs possess different chromatographic properties such as polarity (see section 2.6).

For unsymmetrical Pcs it is essential to establish that there is no cross contamination of products. It is known that *thin layer chromatography* (TLC) is not always completely accurate in resolving small amounts of Pc impurities due to aggregation effects.[20] Therefore, the determination by TLC that a Pc is a 'single spot' must be backed up by other criteria of purity. One of the most useful methods to achieve this is MS. However, normal *electronic or chemical ionisation* (EI/CI) techniques of MS are insufficient to analyse most of these compounds since the molecular weights are consistently in excess of 1000, the upper limit of current EI/CI MS. However, one technique which allows investigation of higher molecular weights is *fast atom bombardment* (FAB) MS since it allows ionisation of samples of low volatility.

Thus, all of the Pcs with molecular weights over 1000 were investigated by FAB MS and most gave a spectrum, this is probably due to the increased solubility of the Pcs compared to unsubstituted phthalocyanine, due to their dendritic substitution. The spectra of the mixed Pcs were found to show no detectable peaks due to other members of their particular series. An example of a FAB MS of a Pc is given for **(9)** in Fig. 1.4.

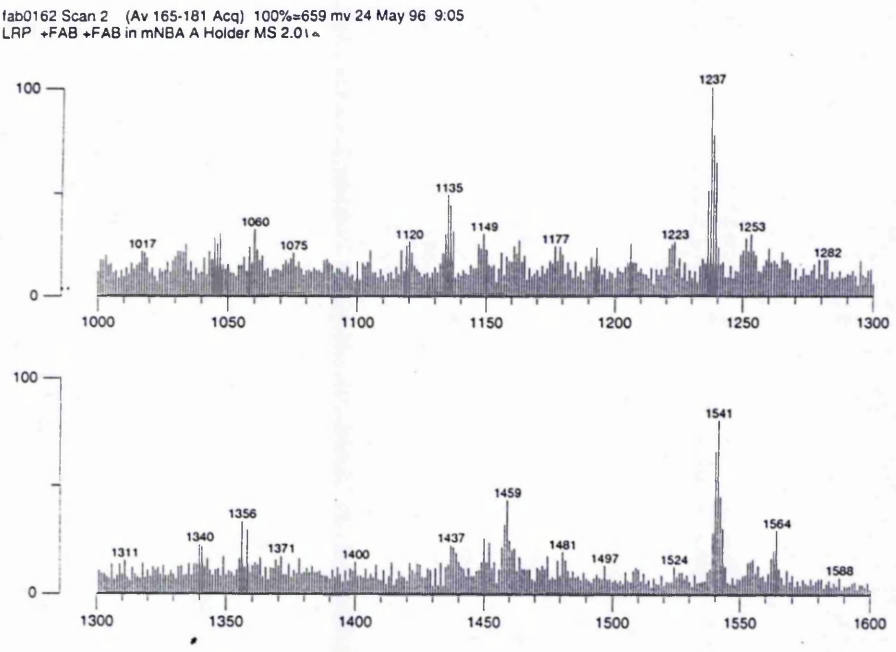


Fig. 1.4 FAB Mass Spectrum of Pc **(9)**

The problem with this method however, is that the level of noise was generally around 5 % of the molecular ion peak (or equivalent) and, it is therefore, by no means complete proof that small amounts of other Pcs are not present. In addition, since MS is a method of molecular weight determination, it is by its very nature incapable of differentiating structural isomers. Additional methods such as *high resolution NMR, matrix assisted laser absorption ionisation* (MALDI) and *high performance liquid chromatography* (HPLC) would be required to confirm the absence of Pc cross-contamination. However, due to the time constraints of this project, the ratios of phthalonitrile in the mixed Pc reactions, were carefully selected such that the product contained virtually only the required phthalocyanine.

1.1.9 Axially Substituted Phthalocyanines

It is possible to attach axial ligands to the central metal (or metalloid) ion of a metal containing Pc (Fig. 2.5). Axial substitution can enhance solubility and help to reduce face to face intermolecular interactions resulting in materials which have interesting optical and photo electronic properties. In general, covalently bound axial ligands require a central metal ion in a M^{3+} or M^{4+} oxidation state. Many such examples exist of axially substituted derivatives of, for example SiPc (see section 2.8.2) and GePc. The group IV metal phthalocyanines are of interest because various groups can be attached to the axial or trans positions.[21] Additionally suitable ligands (e.g. pyridines) form co-ordination bonds with many central metal ions.[22] This accounts for the enhanced solubility of MPcs in pyridine and quinoline.

Axially substituted phthalocyanine compounds often show high thermal and chemical stability and interesting optical and electrical properties.[23, 24, 25, 26, 27]

1.2 Phthalocyanine Material Properties

1.2.1 Mesomorphic Phthalocyanine Materials

Liquid crystals or mesophases (*meso* = Greek for intermediate) lie between the 3-dimensional order of crystalline solids and the disorder of conventional liquids. They are anisotropic materials i.e. have non-uniform physical properties in different directions in which the molecules

have some long range orientational, and maybe some positional ordering. Mesophases are generally categorised into two main groups, thermotropic and lyotropic.

1.2.2 Lyotropic Mesophases

Lyotropic mesophases[28] are induced by the addition of a solvent to an amphiphilic material (a substance which contains hydrophilic and hydrophobic portions), resulting in a system which can be varied by temperature and concentration of solvent. These phases are formed usually because the addition of a polar solvent e.g. water, causes aggregation of non-polar parts of molecules and effectively, micro-phase separation takes place. The most common examples of lyotropic liquid crystalline materials in everyday life are washing-up liquid, shampoo and shower gel.

1.2.3 Thermotropic Mesophases

Thermotropic liquid crystals are materials which undergo phase changes by the action of heat. The property which gives rise to the phenomenon of liquid crystallinity is shape anisotropy of the constituent molecules (or molecular aggregates for lyotropic systems) and therefore, most mesogens are composed of rod or disc shaped molecules (Fig. 1.5).[29] The rods and discs in Fig. 1.5 represent the molecular structure which usually consists of a rigid core such as aromatic units, substituted with flexible side-chains.

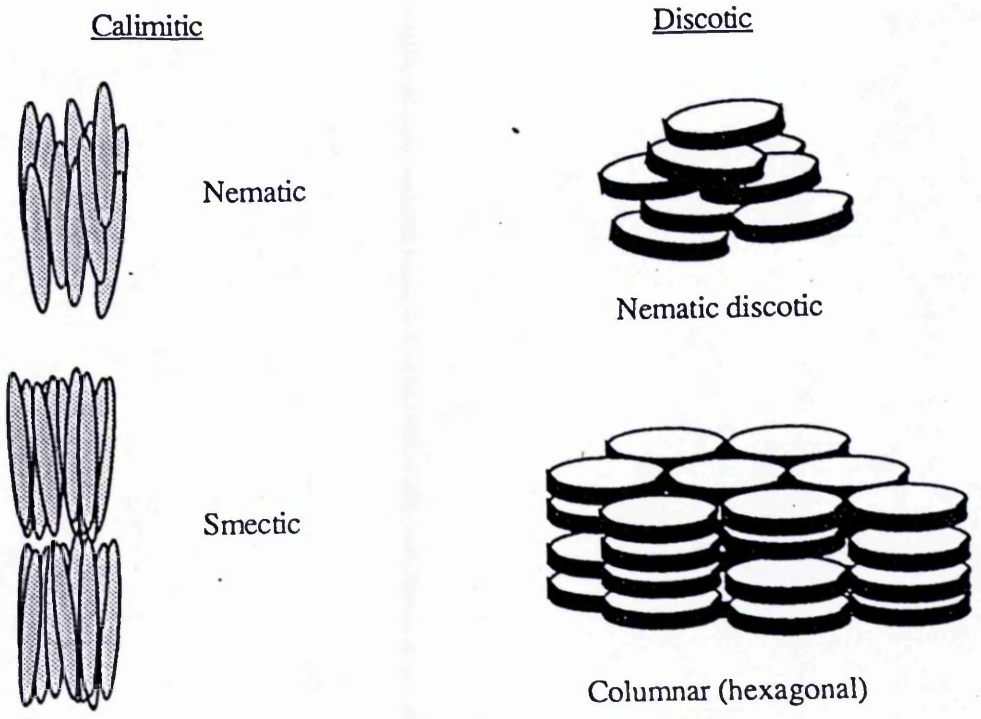


Fig. 1.5 Categories of Thermotropic Liquid Crystals.

The phenomenon of thermotropic liquid crystallinity was originally discovered in rod like or *calamitic* derivatives of cholesterol in 1888 by Reinitzer[30] and since then many thousands of calamitic mesogens have been prepared. Calamitic compounds can display a *nematic* phase, a fluid, turbid phase which often shows a threaded texture when viewed microscopically between crossed polarises. Hence, the name nematic from the Greek *nematos* meaning thread like. In this phase, the molecules possess only imperfect orientational order.

The *cholesteric* mesophase is also a fluid, turbid phase but it exhibits unique optical properties. This phase was originally observed in the derivatives of cholesterol hence its name, although today, most

compounds which exhibit this mesophase are not derivatives of cholesterol.

The *smectic* mesophase is a more viscous, turbid phase in which positional and orientational order combine to give a layered structure. It was named from the Greek *smectos*, meaning soap-like. Originally it was thought that only one type of smectic phase existed, but now a number have been discovered and are known as S_A, S_B, S_C etc, each with slightly different structural arrangements of the molecules and degree of ordering.

Due to shape anisotropy, elongated 'rod-shaped' or flat 'disc-shaped' molecules commonly form liquid crystal mesophases. The type of liquid crystallinity encountered in this thesis are the thermotropic mesophases derived from discotic molecules.

1.2.4 The Discovery of Discotic Liquid Crystals

The first disc-like molecules which exhibited stable mesophases were the hexa-substituted esters of benzene (or hexa-n-alkonates) (Fig. 1.6). They were first identified in 1977 by Chandrasekhar et al.[31, 32]

Optical and X-ray studies revealed that a new kind of mesophase, quite distinct from the classical nematic or smectic types formed by calamitic liquid crystals is formed by these materials. The discs stack on top of each other aperiodically and form liquid like columns.

A number of similar mesogens were found soon afterwards by Dubois,[33] Destrade et al[34] and the basic columnar structure was verified by the X-ray crystallography work of Levelut.[35, 36] Molecules which form discotic liquid crystals usually have rigid, flat cores which normally contain aromatic rings substituted with four, six or eight flexible chains.[36, 37]

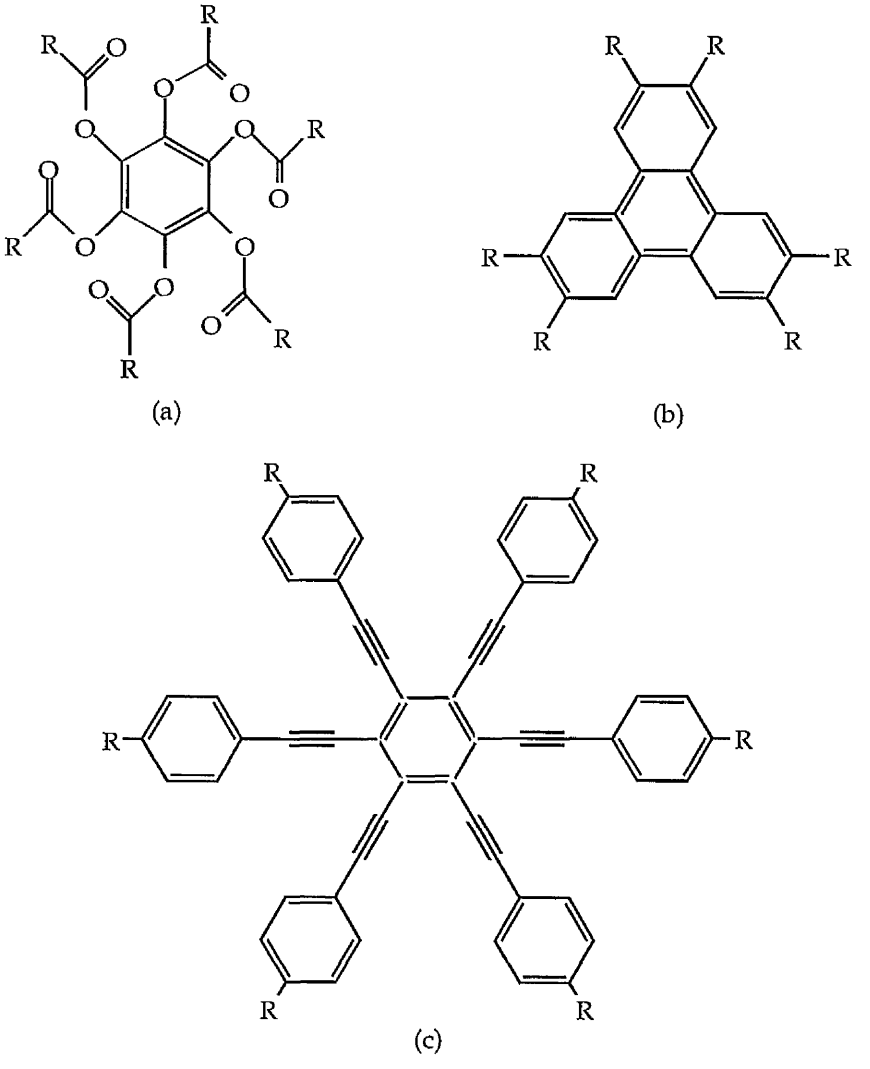


Fig. 1.6 Discotic mesophase forming compounds (discogens)
(a) Hexa-*n*-alkonates of benzene,[31] (b) hexa-*n*-alkonates of triphenylene and hexa-*n*-alkoxytriphenylene,[34, 38] (c) hexakis((4-octylphenyl)ethynyl) benzene.[39]

As shown in Fig. 1.6, the most common chains are alkyl, alkoxy or ester groups of at least five carbon atoms in length.

1.2.5 Columnar Discotic Mesophases

Molecules which are disc-like often show a tendency to stack on top of one another to form columns. This then gives rise to a variety of columnar phases, differing in the degree of order within the columns and also the orientation of the columns with respect to each other, (see appendix 3).

1.2.6 Pc Columnar Liquid Crystals

The ability to form thermotropic columnar liquid crystals can be induced by the peripheral (2, 3, 9, 10, 16, 17, 23, 24) substitution of the Pc macrocycle with eight alkyl,[40] alkoxy,[41] alkoxymethyl,[42] or oligo(ethyleneoxy)[43] side-chains. Similar behaviour is demonstrated by derivatives with eight alkyl or alkoxymethyl[44] substitution at the non-peripheral (1, 4, 8, 11, 15, 18, 22, 25) sites. In addition, a number of unsymmetrically substituted Pcs have been shown to form thermotropic liquid crystals.[45] Consequently, this has led to mesogenic derivatives which can be incorporated into oligomers[46] and polymers,[47] or which possess an amphiphilic structure and thus, the ability to form well structured LB films.[15] The introduction of water solublising groups onto the peripheral sites of the Pc gives rise to lyotropic crystallinity owing to the formation of columnar aggregates in concentrated aqueous solution.[48] Recent research within our laboratory has shown that peripherally

attached oligo(ethyleneoxy) moieties produce Pcs which form columnar lyotropic mesophases in pure water, in addition to thermotropic columnar phases.[49] Pcs substituted with oligo(ethyleneoxy) groups are also of interest as ionic conducting materials.[13]

1.2.7 Mesophase Characterisation

Mesophase characterisation is usually carried out using a polarising microscope in conjunction with a hot-stage to control sample temperature. The microscope texture or birefringent appearance is characteristic of the type of mesophase,therefore tentative structural assignments can be made by using this technique.

Differential scanning calorimetry (DSC) can also be used to give transition temperatures. This technique also measures the change in enthalpy (ΔH_t) associated with the transitions which leads to information of the relative order of molecules within the phases. A large value for ΔH_t suggests that there is a large difference in structural ordering between the two phases.

For Pc mesogens, generally crystalline solid to mesophase transitions associated with the melting of the flexible side-chains have a larger value of ΔH_t than mesophase to isotropic liquid transitions. Mesophase to mesophase transitions may also have ΔH_t values, but these are usually smaller and are generally not observable by DSC. A glass transition temperature (Tg), the temperature at which the Pc undergoes the transformation from an isotropic liquid or a liquid crystal to a glass[50] without crystallisation, or an associated change in its birefringent texture,

can also be readily determined by DSC analysis.

X-ray diffraction (XRD) is an excellent technique which can be used for columnar mesophase structure determination (see appendix 2). The technique gives diffraction patterns which are based upon the repeat distances of the columnar lattice arrangements.[51, 52] Much more structural information can be obtained from uniformly oriented samples, however, the fact that the mesophases displayed by Pc derivatives are of a highly viscous nature can make alignment in a single domain difficult. Therefore, most XRD studies have been carried out on a non-oriented (powder) samples. Mesophase structural assignments which are deduced only from microscopic textures are questionable.

1.3 Pc Mesogen Structure-Property Relationships

1.3.1 The Number and Type of Flexible Side-Chains

Many examples of symmetrically substituted Pc mesogens substituted with eight, or more rarely four flexible side-chains have been synthesised. Also some non-uniformly substituted mesogenic derivatives which contain eight, seven, six, five and four alkyl groups are known.[53, 54]

Both alkyl and oligo(oxyethylene) flexible side-chains can be used to induce Pc mesogenicity. A direct comparison between two Pcs substituted with either eight alkyl or eight oligo(oxyethylene) chains shows that the alkyl substituted Pc has a higher crystal to mesophase transition and a higher clearing point (mesophase to isotropic transition) than its

oligo(oxyethylene) substituted analogue.[53] The former difference reflects the higher melting point of alkyl compared to oligo(oxyethylene) chains and the latter difference is probably due to the greater rigidity of alkyl chains which would enhance the disc-shape anisotropy and, therefore, extend thermal stability of the mesophase.

1.3.2 The Effect of Side-Chain Length

Generally if a Pc is substituted with straight alkyl chains of four or fewer atoms in length, it will not possess a mesophase, but will melt directly from its crystalline state into an isotropic liquid at elevated temperatures. Pcs substituted with alkyl chains of moderate length (five to eight atoms) possess initial melting temperatures which are very dependent on the chain length, longer chains will reduce the crystal to mesophase transitions considerably. However, for Pcs with side chains longer than eight atoms, there is no clearly defined relationship between side chain length and the temperature of the initial melting transition, but once again increasing length and bulkiness of the side-chain reduces the temperature of the crystal to mesophase transition.

1.3.3 The Effect Of linking Group and the Site of Substitution

The linking groups are defined as the first two atoms in the chain next to the Pc ring. The steric and electronic effects of the group that link the alkyl chains to the Pc ring can result in different transition temperatures and some difference in the structure of the resulting columnar mesophase.[55]

For example, molecular modelling calculations show that the relatively small alkoxy linking group allows the side chains to sit comfortably in the plane of the ring, but the steric crowding of alkyl and alkyloxymethyl groups results in a conformation tilted by 35 ° to the plane of the ring.[56] Hence, the alkoxy linking group favours hexagonal columnar mesophases (D_{ho}), but no tilted mesophases are observed for straight side-chain octa-alkyl derivatives.

1.3.4 The Formation of Pc Glasses

Pc molecules within a columnar mesophase rotate rapidly about the columnar axis. A number of studies have been performed to try to prevent this axial rotation and produce a material which may be oriented in a columnar mesophase and then frozen into a non-crystalline *glassy* state. It has been suggested that suppression of the solid crystalline state in which the Pc molecules usually adopt a tilted arrangement and lose the extensive π–π orbital overlap could improve intrinsic conductivity. Anisotropic glassy states are commonly encountered in calamitic side-chain liquid crystal polymers and have been achieved for polymeric discotic triphenylene systems, but side-chain polymers incorporating Pc mesogens have failed to show mesogenic behaviour.[57] However, mesogenic Pcs with polymerisable groups located at the end of the flexible side-chains[57] allow the formation of the columnar mesophase. The mesophase is frozen into a stable solid state by light induced polymerisation of the end-groups.

Structural factors which influence the formation of glasses from discotic phases in monomeric compounds cannot be fully explained from the molecular origin. However, two general factors are thought to contribute to the formation of amorphous glassy materials rather than crystalline solids in polymers. Stereochemistry has a large effect on the presence and extent of crystallinity, tactic or stereoregular polymers tend to be crystalline in nature, whereas atactic polymers tend to be amorphous. The bulkiness of the side group also has an effect, usually polymers with bulky groups tend not to crystallise as easily as those without, and consequently are more likely to be amorphous.

Isotropic glassy solids are produced when bulky groups are placed directly onto a Pc without the flexible spacer group,[58] or, as described latter in this thesis, by using axially substituted dendrimers (Fig. 2.5). For the former system, cofacial association is apparent from the UV/vis absorption spectrum. It was originally envisaged that dendritic substitution of Pc would produce materials in which the macrocyclic core would be sterically isolated. Consequently, these clear, non-scattering *solid solutions* may be of interest for their optical properties.

1.4 Dendrimers : From Generations and Functional Groups to Functions

There is a growing interest in macromolecules with architectures which differ from those of classical linear polymers, as new polymer architectures may exhibit unusual behaviour and possess different properties.[59] One family of macromolecules which has attracted

considerable attention is that of the dendritic macromolecules, compounds which are characterised by a large number of terminal groups all emanating from a central core with at least one branch at each repeat unit.

When a new idea is particularly appealing, activity in that area may be almost epidemic.[60] A recent example of this is the development of dendrimer work since 1990. Until recently, the primary goal was the synthesis of dendrimers with high molecular mass and as many generations as possible, but in the last few years, the emphasis has changed and the synthesis of large complex molecules has become less important. A first indication of the new trends in dendrimer research was a report by Newkome *et al* [61] on a chiral dendrimer. In 1992 Shinkai *et al* described a 'crowned arboral' capable of complexing metal ions with the crown ether units at the periphery of the molecule[62] and Vögtle *et al* developed a reversibly photoswitchable dendrimer containing terminal azabenzene units.[63]

These first examples of cascade molecules with functional components point at the new direction of dendrimer research i.e. properties are being modified increasingly with functional centres. Not the dendrimer itself, but the multiplication of functional components attached to a dendritic skeleton and new materials with specific properties (redox behaviour, metal-ion complexation, liquid crystal properties and biochemical activity) are anticipated. Industry has also shown an increasing interest in functional cascade molecules for applications in diverse areas such as medical engineering[64] agrochemistry,[65] and the development of photocopier toners.[66, 67] Furthermore, the potential of dendrimers in pharmaceutical and medical applications,[68] diagnostic imaging,[69] and

radiation therapy[70, 71] is frequently discussed.

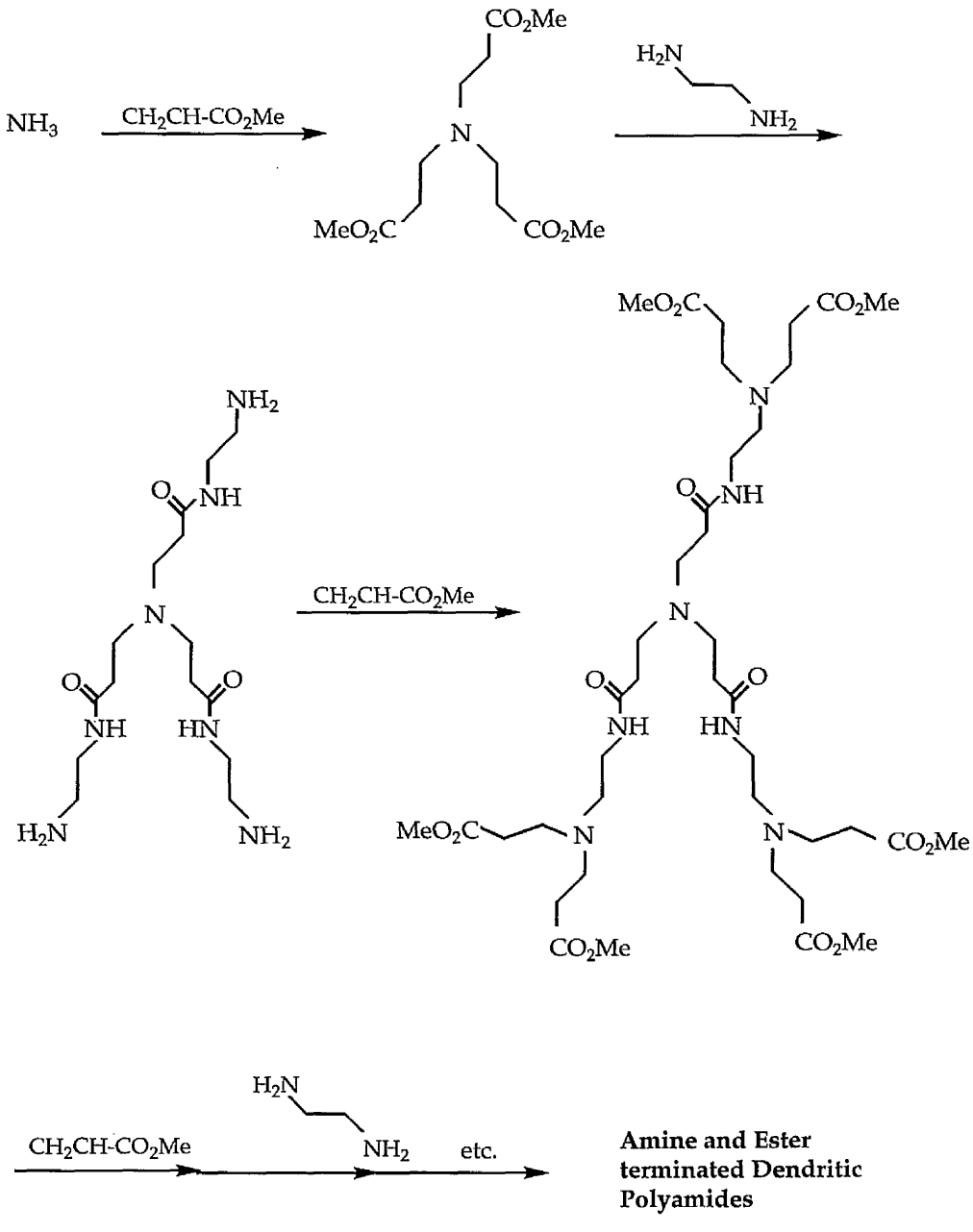
1.4.1 Dendrimer Synthesis

Dendrimers have received considerable synthetic[72, 73, 74, 75, 76, 77] and theoretical[78, 79, 80, 81,] attention recently. Perhaps the earliest relevant examples of such highly branched structures are the 'cascade' molecules of Vögtle [72] which had relatively low molecular weights. Later and almost simultaneous work by Tomalia[73, 74] and Newkome[75, 76] produced truly macromolecular hyperbranched polymers, such as the 'starburst' polymers. The interest in these macromolecules is due to their novel, highly branched, globular structures that are reminiscent of many important biological molecules. The discovery of new phenomena or new properties may be expected from the study of these uniquely shaped and non-entangled macromolecules.

1.4.2 Approaches to Monodisperse Dendritic Macromolecules

Previous synthetic work[73, 74, 75, 76, 77] had primarily been directed towards the synthesis of dendritic macromolecules by a *divergent growth* methodology. In these cases growth occurs from a central core by successive stepwise addition and activation steps which multiply the number of branches. In Tomalia's case[73] methyl acrylate and ammonia, followed by exhaustive amidation of the resulting esters with a large excess of ethylenediamine, affords the next generation of reactive amine groups, (Scheme 1.4). Repetition of the two-step procedure leads to

subsequent generations. A significant feature of this methodology is the rapid increase in the number of reactive groups at the periphery of the growing macromolecule.



Scheme 1.4 The *divergent* approach to dendrimer synthesis.

Potential problems which may arise as growth continues include incomplete reaction of these terminal groups, which would lead to imperfections in the next generation, the probability of this occurring increases with the growing macromolecule. Secondly the large excess of reagents that are required to force the reaction to completion in the latter stages of growth, presents difficulties in purification. This lead to the proposal of a *convergent growth* [82, 83] methodology, which overcomes these problems and can be used for different families of structures.

Using the symmetrical nature of these molecules to advantage, construction of the molecule starts from what will become the extremities of the chains or 'periphery' of the spheroidal molecules using a convergent approach (Scheme 2.1). Each successive generation is then synthesised in step-wise fashion producing a new dendritic molecule in which a single reactive group located at the focal point of all branches is used in further growth. The final reaction involves the attachment of a complete dendrimer 'wedge' to a polyfunctional core molecule, to afford a spheroidal dendritic macromolecule.

The convergent approach offers a number of features less readily accessed by the divergent approach, such as control over surface functionality,[84] involvement of a very limited number of reactive sites (typically three) for generation growth, essentially monodisperse products and ease of purification and characterisation. However, one limitation of the convergent approach is that as the size of the dendrimers increase, they are increasingly more susceptible to steric hindrance at the focal point group. This limitation is not as significant as with the divergent approach, though a similar steric constraint is reported as 'dense packing'.[85]

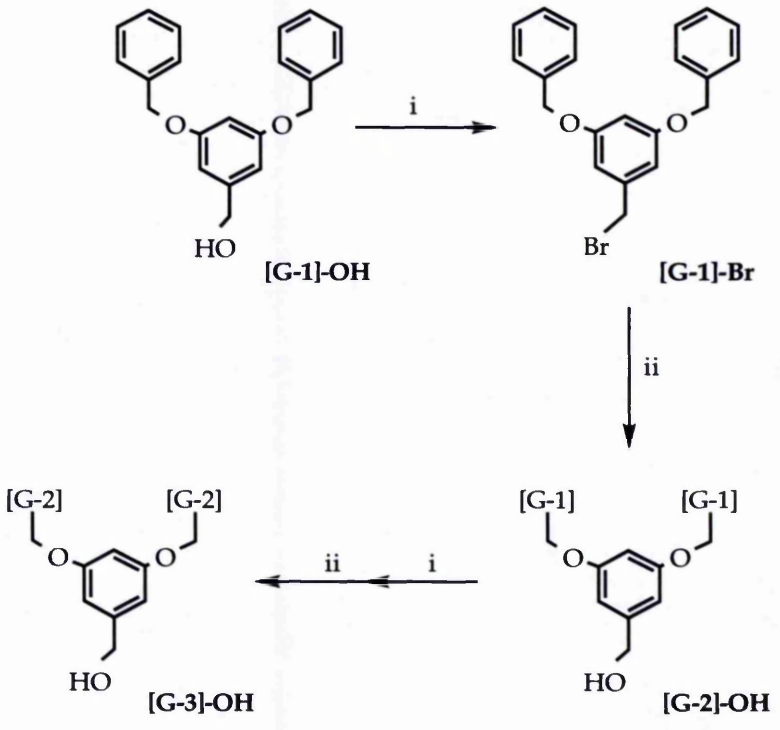
To allow higher molecular weight products of low polydispersity to be prepared in multigram quantities, a novel 'double-stage' convergent approach was proposed.[86] In this process, a dendritic molecule which carries at least one reactive functional group at each of its numerous chain extremities is prepared by the convergent growth approach, and is then used as a core to attach other preformed dendritic fragments through their single focal point reactive group.[82]

A particular feature of this technique is that the inner hyperbranched core, *'hypercore'* may be constituted of flexible segments, providing ample spacing between the reactive groups at each end. As a result the coupling of dendritic fragments to this loose hypercore is facilitated, and less subject to the steric constraints encountered with more compact cores of three phenolic functionalities linked to a single tetrahedral carbon atom.

A further exploitation of the convergent methodology is the accelerated synthesis of regular dendritic macromolecules.[87] Based on the concept that with the proper choice of monomers, it should be possible to grow two generations in one synthetic operation, without the need for purification or activation. Hence, the synthesis of a third generation dendrimer directly from first generation material with only a single purification step, in comparison to the four purification and two activation steps required for the conventional growth of two generations is possible (Scheme 1.5).

A fundamental difference between dendritic and linear polymers is the bonding and branching sequence. Dendritic macromolecules contain a large number of symmetrically arranged branches that originate from a

central point, a branch point at each monomer unit, and a large number of chain ends or surface functional group. These factors result in three-dimensional globular structures, which posses new and unusual characteristics such as the absence of classical entanglements found in linear polymers.



Scheme 1.5 'Two-step approach' to accelerated dendrimer synthesis.

At high molecular weights, these structures may approximate spheres and as generations increase, molecular weight increases rapidly, without much

change in the size of the dendrimer. In comparison to a linear polymer of the same molecular weight the dendritic polymer will have a lower viscosity.

1.4.3 Molecular Architecture of Dendritic Macromolecules

The globular shape of the dendritic macromolecules should be relatively fixed, in contrast to linear polymers which are random coils and, depending on the solvent, may vary in shape and size from extended to compact coils. This retention of structure in solution has been exploited by Newkome in a paper describing unimolecular micelles prepared by the divergent growth approach.[88] These unimolecular micelles are a new class of dendritic macromolecules where an interior hydrophobic core is surrounded by a hydrophilic surface layer. In Newkome's system there is a branching hydrocarbon interior consisting of two generations of nonyl units which is surrounded by a hydrophilic surface layer consisting of 36 carboxylate chain ends. The structure closely resembles that of a micelle except that it is static with all carboxylate or head groups covalently linked to a central core. Therefore, unlike traditional micelles, the structure would be expected to retain its cohesion over the entire range of concentrations and in a greater variety of solvents. Characterisation of this novel macromolecule did indeed show that it existed as a single molecule capable of molecular inclusion.[89]

It has been shown that a degree of control can be obtained over the nature and functionality of both the internal building blocks[89] and the chain ends[90] in the convergent synthesis of dendritic macromolecules. This approach also allows precise control over the monomer units in the interior of the dendritic macromolecule. These combined abilities allow the synthesis of novel dendritic *block* copolymers, which extend further the increasingly important fields of both dendritic macromolecules and block copolymers. Traditional block copolymers are important since they often exhibit useful and unique properties in solution and the solid state due to the general thermodynamic incompatibility of the blocks. They are usually composed of linear blocks, however, due to the three-dimensional nature of dendritic macromolecules, there are a number of different architectures which can result in dendritic block copolymers.[90]

As previously mentioned, dendrimers are highly branched three-dimensional macromolecules with a branch point at each monomer unit. Therefore, they are potentially the most highly branched structures that exist. As a result of this high degree of branching , large dendrimers adopt a globular shape in which all bonds converge to a focal point or central core unit. Of particular interest in the context of functional polymers is the fact that dendrimers possess a very large number of chain ends. For example the dendrimers prepared by Fréchet *et al* (Scheme 2.1), have two branches at each monomer unit and, therefore possess the same number of chain ends as they have monomer units. The synthesis itself proceeds in steps, with each addition of monomer (a generation growth step), resulting essentially in the doubling of both the mass of the dendrimer and the number of its chain ends.

The steric considerations that dictate the globular shape of the dendrimers also affect their ability to interact with neighbouring molecules. A macroscopic analogy for comparison of linear polymers and dendrimers is 'cooked spaghetti' and 'green peas', the former relatively entangled and the latter not.

1.4.4 Physical Properties of Dendritic Macromolecules

Due to their shape, dendrimers have very unusual physical as well as chemical properties.[91, 92, 93] As the molecular weight increases within a homologous series of dendrimers, the molecules undergo a transition from an extended to a globular shape. This transition can be readily observed in a plot of intrinsic viscosity versus molecular weight (Fig. 1.7).[91]

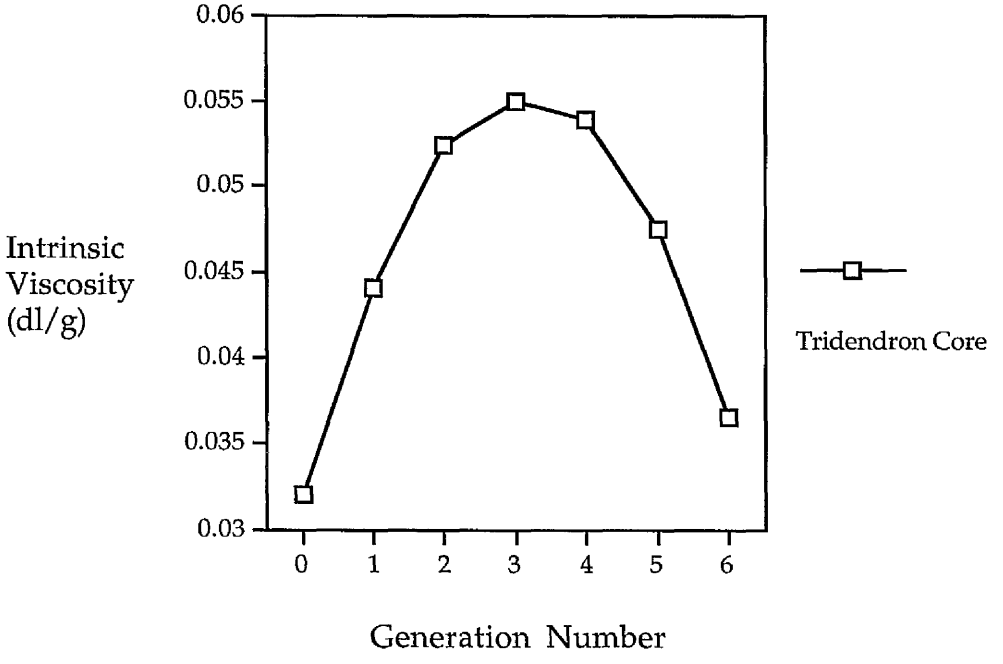


Fig. 1.7 Plot of intrinsic viscosity versus generation number for typical polyether dendrimers.[94]

For classical linear polymers such as poly(styrene), the viscosity increases sharply with molecular weight, according to the Mark-Houwink-Sakurada equation

$[\eta] = K M^{a}$ where η is the intrinsic viscosity of the polymer
M is the molecular weight
K and a are constants for a given polymer.

Unlike almost all other macromolecules, including branched and star polymers, dendrimers do not obey this relation once a threshold molecular weight is reached. This is easily understood because during generation growth, the molecular weight of the dendrimers increase cubically, whilst their volume increases exponentially, a relationship that does not hold true for other polymers.

Having established that large dendrimers acquire a globular shape, it is interesting to compare their properties with those of linear polymers consisting of essentially the same building blocks.[94] It was concluded that the solubility of a dendrimer is remarkably high compared to that of an analogous size linear polymer, and there is also a marked difference in chemical reactivity with the dendrimer being more reactive in the catalytic hydrogenolysis with a solid Pd/C catalyst and hydrogen gas. Although alternative explanations are possible, it is tempting to associate the unusually high solubility and reactivity of the dendrimer when compared to its linear analogue to the global architecture of the former.

1.5 Aims of this Thesis

This thesis investigates phthalocyanines substituted with dendrimers of varying generation either peripherally, in an attempt to produce anisotropic structured glassy solids, or axially, to form isotropic glasses. The synthesis of the aryl ether dendrimers was to be achieved using the convergent method developed by Fréchet *et al* .[81]

1.6 Chapter One References

1. Braun, A., Tcherniac, J., *Ber. Deut. Chem. Ges.*, 1907, 40, 2709
2. de Diesback, H., von der Weid, E., *Helv. Chim. Acta.*, 1927, 10, 88
3. Dandridge, A. G., Drescher, H. A. E., Thomas, J., *British Patent*, 1928, 332, 169
4. Byrne, G. T., Linstead, R. P., Lowe, A. R., *J. Chem. Soc.*, 1934, 1016
5. Linstead, R. P., Lowe, A. R., *J. Chem. Soc.*, 1934, 1022
6. Dent, C. E., Linstead, R. P., Lowe, A. R., *J. Chem. Soc.*, 1934, 1033
7. Elvidge, J. A., Linstead, R. P., *J. Chem. Soc.*, 1955, 3536
8. Dent, C. E., Linstead, R. P., *J. Chem. Soc.*, 1934, 1027
9. Robertson, J. M., *J. Chem. Soc.*, 1935, 615
10. Robertson, J. M., *J. Chem. Soc.*, 1936, 1195
11. Robertson, J. M., Woodward, I., *J. Chem. Soc.*, 1937, 219
12. Leznoff, C. C., in '*Phthalocyanines - Properties and Applications,*' Eds. C. C. Leznoff and A. B. P. Lever, VCH, New York, Vol. 1, Chapter 1, 1989
13. Simon, J., Bassoul, P., in '*Phthalocyanines - Properties and Applications,*' Eds. C. C. Leznoff and A. B. P. Lever, VCH, New York, Vol. 2, 1992, 223
14. Ulman, A., *Introduction to Ultra Thin Films*, Academic Press, San Diego, 1991
15. Chambier, I., Cook, M. J., Cracknell, S. J., McMurdo, J., *J. Mater. Chem.*, 1993, 3, 841
16. Moser, F. H., Thomas, A. L., '*The Phthalocyanines,*' Vol. 1, *Properties*, CRC Press, Boca raton, FL, 1983
17. Kovshev, E. I., Puchnova, V. A., Luk'yanets, E. A., *Zhurnal Organisch Khimii*, 1971, 7, 369-71
18. McKeown, N. B., Chambrier, I., Cook, M. J., *Journal of the Chemical Society, Perkin Trans. 1*, 1990, 1169-77

19. Clarkson, G. J., McKeown, N. B ., Treacher, K. E., *Journal of the Chemical Society, Perkin Trans. 1*, 1995, 1817-23

20. Leznoff, C. C., Greenberg, S., Khouw, B., Lever, A. B. P., *Can. J. Chem.*, 1987, 65, 1705

21. Krueger, P. C., Kenney, M. E., *J. Org. Chem.*, 1963, 28, 3379

22. Cariati, F., Galizzioli, D., Morazzoni, F., Busetto, C., *Journal of the Chemical Society, Dalton Transactions*, 1975, 556-61

23. Lever, A. B. P., *Adv. Inorg. Chem. Radiochem*, 1965, 7, 27

24. Grammatica, S., Mort, J., *Appl. Phys. Lett.*, 1981, 38, 445

25. Mizuguchi, J., *Jpn. J. Appl. Phys. Lett.*, 1981, 20, 293

26. Kuznesof, P. M., Nohr, S., Wynne, K. J., Kenney, M. E., *J. Macromol. Sci.*, 1981, A16, 299

27. Lever, A. B. P., Licoccia, S., Ramaswamy, B. S., Kandil, A., Styres, D. V., *Inorg. Chim. Acta.*, 1980, 51, 169

28. Hiltrop, K., in *'Topics in Physical Chemistry, Vol. 3 - Liquid Crystals'* Ed. H. Stegemeyer, Steinkopff (Darmstadt), 1994, 143-173

29. Chandrasekhar, S., in *'Liquid Crystals'* 2nd Edition, Cambridge University Press, 1992

30. Reinitzer, F., *Montasch der Wiener Chem. Ges.*, 1888, 9, 421

31. Chandrasekhar, S., Sadashiva, B. K., Suresh, K. A., *Pramana*, 1977, 7, 471

32. Chandrasekhar, S., Sadashiva, B. K., Suresh, K. A., Kumar, S., Shashidar, R., Venkatesh, J., *J. Phys.* (Paris), 1979, 40, 120

33. Dubois, J. C., *Ann. Phys.*, 1978, 3, 131

34. Destrade, C., Mondon, M. C., Malthete, J., *J. Physique. Coll.*, 1979, 40, C3-17

35. Levelut, A. M., *J. Phys. Lett. Paris*, 1979, 40, L-81

36. Levelut, A. M., *J. Chem. Phys.*, 1983, 88, 149

37. Destrade, C., Foucher, P., Gasparoux, H., Tinh, N. H., Levelut, A. M., Malthete, J., *Mol. Cryst. Liq. Cryst.*, 1984, 106, 121

38. Billard, J., Dubois, J. C., Tinh, N. H., Zann, A., *Nouv. J. Chim.*, 1978, 2, 535

39. Kohne, B., Praefcke, K., *Chimia*, 1987, 41, 196

40. Ohta, K., Jacquemin, L., Sirlin, C., Bosio, L., Simon, J., *Nouv. J. Chim.*, 1978, 2, 535

41. Masurel, D., Sirlin, C., Simon, J., *Nouv. J. Chim.*, 1988, 12, 751

42. Piechocki, C., Simon, J., Skoulios, A., Guillon, D., Weber, P., *J. Am. Chem. Soc.*, 1982, 104, 5245

43. Guillon, D., Skoulios, A., Piechocki, C., Simon, J., Weber, P., *Mol. Cryst. Liq. Cryst.*, 1983, 100, 275

44. Cammidge, A. N., Cook, M. J., Harrison, K. J., McKeown, N. B., *J. Chem. Soc., Perkin. Trans. 1*, 1991, 3053

45. Piechoki, C., Simon, J., *J. Chem. Soc. Chem. Commun.*, 1985, 259

46. Bryant, G. C., Cook, M. J., Haslam, S. D., Richardson, R. M., Ryan, T, G., Thorne, A. J., *J. Mater. Chem.*, 1994, 4, 1153

47. Van der Pol, J. F., Neeleman, E., Nolte, R. J. M., Zwikker, Z. W., Drenth, W., *Makrmol. Chem.*, 1989, 190, 2727

48. Usoltseva, N. V., Bykova, V. V., Kormiltsyn, N. M., Ananieva, G. A., Maizlish, V. E., *Il Nuovo Cimento*, 1990, 12, 1237

49. McKeown, N. B., Painter, J., *J. Mater. Chem.*, 1994, 4, 1153

50. Young, R. J., Lovell, P. A., '*Introduction to Polymers*' Chapman and Hall, London, Ed. 2, 1991, 292

51. Cherodian, A. S., Davies, A. N., Richardson, R. M., Cook, M. J., McKeown, N. B., Thomson, A. J., Feinjoo, J., Ungar, G. & Harrison, K. J., *Molecular Crystals and Liquid Crystals*, 1991, 196, 103-14

52. Simon, J., Engel, M. K. & Soulié, C., *New Journal of Chemistry*, 1992, 16, 287-93

53. Treacher, K. E., PhD thesis, University of Manchester, 1995

54. Humberstone, P., PhD thesis, University of Manchester, 1996

55. Weber, P., Guillon, D., Skoulios, A., *Liquid Crystals*, 1991, 9, 369-82

56. Van der Pol, J. F., Neeleman, E., Zwikker, J. W., Nolte, R. J. M., Drenth, W., *Recueil des Travaux Chimiques des Pays-Bas*, 1988, 107, 615-620

57. Van der Pol, J. F., Neeleman, E., Nolte, R. J. M., Zwikker, J. W., Drenth, W., *Makromolekulare Chemie, Macromolecular Chemistry and Physics*, 1989, 190, 2727-45

58. George, R. D., Snow, A. W., *Chemistry of Materials*, 1994, 6, 1587-8

59. Bikales, N. M., *Polymn. J.*, 1987, 19, 11

60. Braun, T., *Angew. Chem.*, 1992, 104, 602

61. Newkome, G. R., Liu, X., Weis, C. D., *Tetrahedron Asymmetry*, 1991, 2, 957

62. Nagasaki, T., Ukon, M., Arimori, S., Shinkai, S., *J. Chem. Soc. Chem. Commum.*, 1992, 608-610

63. Mekelburger, H. B., Rissanen, K., Vögtle, F., Chem. Ber., 1993, 126, 1161-1169

64. Haenseler, J., Szoka, F., *Bioconjugate Chem.* 1993, 4, 372-379

65. Tomalia, D. A., Wilson, L. R., *Chem. Abstr.* 1993, 120, 256197

66. Winnik, F. M., Davidson, A. R., Breton, M. P., *Chem. Abstr.*, 1992, 117, 133079p

67. Winnik, F. M., Duff, J. M., Sacripante, A. R., Davidson, A. R., *Chem. Abstr.* 1993, 120, 90707j

68. Pappas, N. A., Argade, A. B., *Chem. Abstr.* 1993, 120, 72540v

69. Tomalia, D. A., Wilson, L. R., *Chem. Abstr.* 1993, 120, 256197

70. Barth, R. F., Adams, D. M., Soloway, A. H., Alam, F., *Chem. Abstr.* 1994, 120, 86391j

71. Barth, R. F., Adams, D. M., Soloway, A. H., Alam, F., *Chem. Abstr.* 1993, 118, 3077w

72. Buhleier, E., Wehner, W., Vögtle, F., *Synthesis,* 1978, 155

73. Tomalia, D. A., Baker, H., Dewald, J., Hall, M., Kallos, G., Martin, S., Roeck, J., Ryder, J., Smith, P., *Polym. J., (Tokyo)* 1985, 17, 117

74. Tomalia, D. A., Baker, H., Dewald, J., Hall, M., Kallos, G., Martin, S., Roeck, J., Ryder, J., Smith, P., *Macromolecules,* 1986, 19, 2466

75. Newkome, G. R., Yao, Z., Baker, G. R., Gupta, V. K., *J. Org. Chem.,* 1985, 50, 2004

76. Newkome, G. R., Yao, Z., Baker, G. R., Gupta, V. K., Russo, P. S., Saunders, M. J., *J. Am. Chem. Soc.,* 1986, 108, 849

77. Padias, A. B., Hall, H. K., Tomalia, D. A., McConnell, J. R., *J. Org. Chem.,* 1987, 52, 5305

78. de Gennes, P. G., Hervet, H. J., *J. Phys. Lett.,* 1983, 44, 351

79. Burchard, W., Kajaiwara, K., Nerger, D., *J. Polymn. Sci., Polymn. Phys. Ed.,* 1982, 20, 157

80. Maciejewski, M., *J. Macromol. Sci., Chem.,* 1982, 17, 689

81. Naylor, A. M., Goddard, W. A., Tomalia, D. A., *J. Am. Chem. Soc.,* 1980, 111, 2339

82. Hawker, C. J., Fréchet, J. M. J., *J. Am. Chem. Soc.,* 1990, 112, 7638

83. Hawker, C. J., Fréchet, J. M. J., *J. Am. Chem. Soc., Chem. Commun.,* 1990, 1010

84. Hawker, C. J., Fréchet, J. M. J., *Macromolecules* 1990, 3, 4726

85. Tomalia, D. A., Naylor, A. M., Goddard, W. A., III. *Angew. Chem. Int. Eng. Ed.,* 1990, 29, 138

86. Hawker, C. J., Fréchet, J. M. J., *J. Am. Chem. Soc.,* 1991, 113, 4252

87. Spindler, R., Fréchet, J. M. J., *J. Chem. Soc. Perkin Trans. 1,* 1993, 913

88. Newkome, G. R., Moorefield, C. N., Baker, G. R., Johnson, A. L., Behera, R. K., *Angew. Chem., Int. Ed. Engl.*, 1991, 30, 1176

89. Kim, Y. H., Webster, O. W., *J. Am. Chem. Soc.*, 1990, 112, 4592

90. Hawker, C. J., Fréchet, J. M. J., *J. Am. Chem. Soc.*, 1992, 114, 8405

91. Tomalia, D. A., Dupont-Durst, H., *Top. Curr. Chem.*, 1993, 165, 193

92. Mourey, T. H., *Macromolecules,* 1992, 25, 2401

93. Gitsov, I., Wooley, K., Hawker, C. J., Ivanova, P. T., Fréchet, J. M. J., *ibid.*, 1993, 26, 5621

94. Fréchet, J. M. J., *Science,* 1994, 263, 1710

2

Synthesis and Characterisation of Novel Dendritic Phthalocyanines

2.1 Synthesis of Dendritic Phthalonitrile Precursors

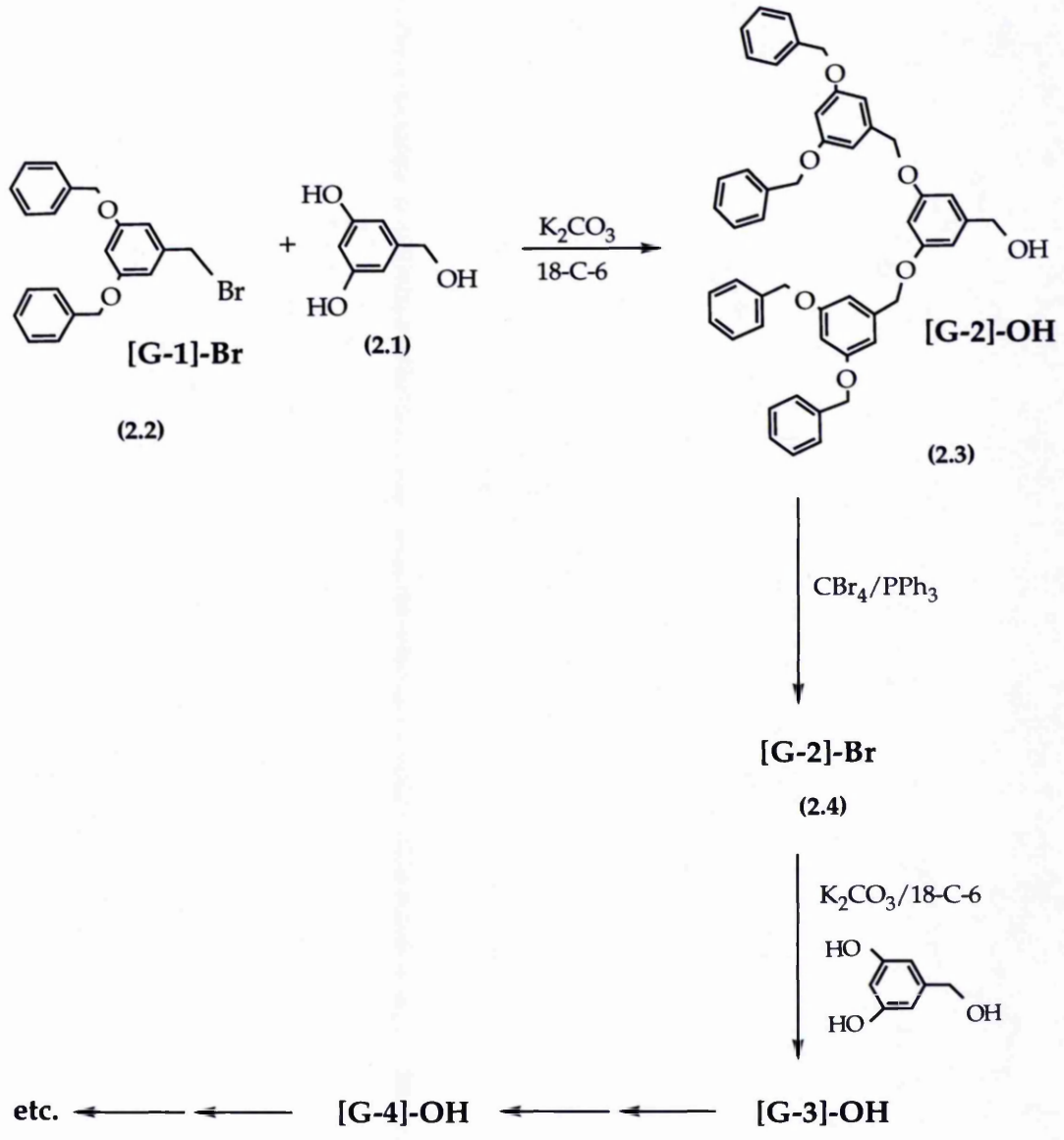
2.1.1 Synthesis of Dendrimer Fragments

As previously mentioned, dendrimer synthesis can be achieved by either the *divergent* [1, 2, 3, 4, 5] or *convergent* [6] approach. A series of dendritic alcohols were prepared by the 'convergent-growth' method utilising 3,5-dihydroxybenzyl alcohol as the monomer unit.[6, 7] The various generation dendritic molecules are designated by using [G-X]-f, where [G-X] refers to the generation number (X = 0, 1, 2, 3) and f refers to the functional group located at the focal point.

2.1.2 Synthesis of a series of Benzyl Aryl Ether Dendrimers with Hydroxymethyl Focal Functionality

Williamson coupling of the monomer unit (**2.1**) with the known benzylic bromide[8] (**2.2**) was found to occur readily in the presence of potassium carbonate and 18-crown-6. The dendritic fragment (**2.3**) was obtained in high yield and was easily purified. Alkylation of the monomer unit (**2.1**) occurs regioselectively at the phenolic hydroxy group, leaving the focal functionality, the hydroxymethyl group available for further modifications. Reaction of this group with carbon tetrabromide and triphenylphosphine regenerates the reactive bromomethyl group (**2.4**).

Repetition of this simple two-step alkylation/bromination procedure affords monodispersed dendritic macromolecules with a single functionality at the focal-point (Scheme 2.1).



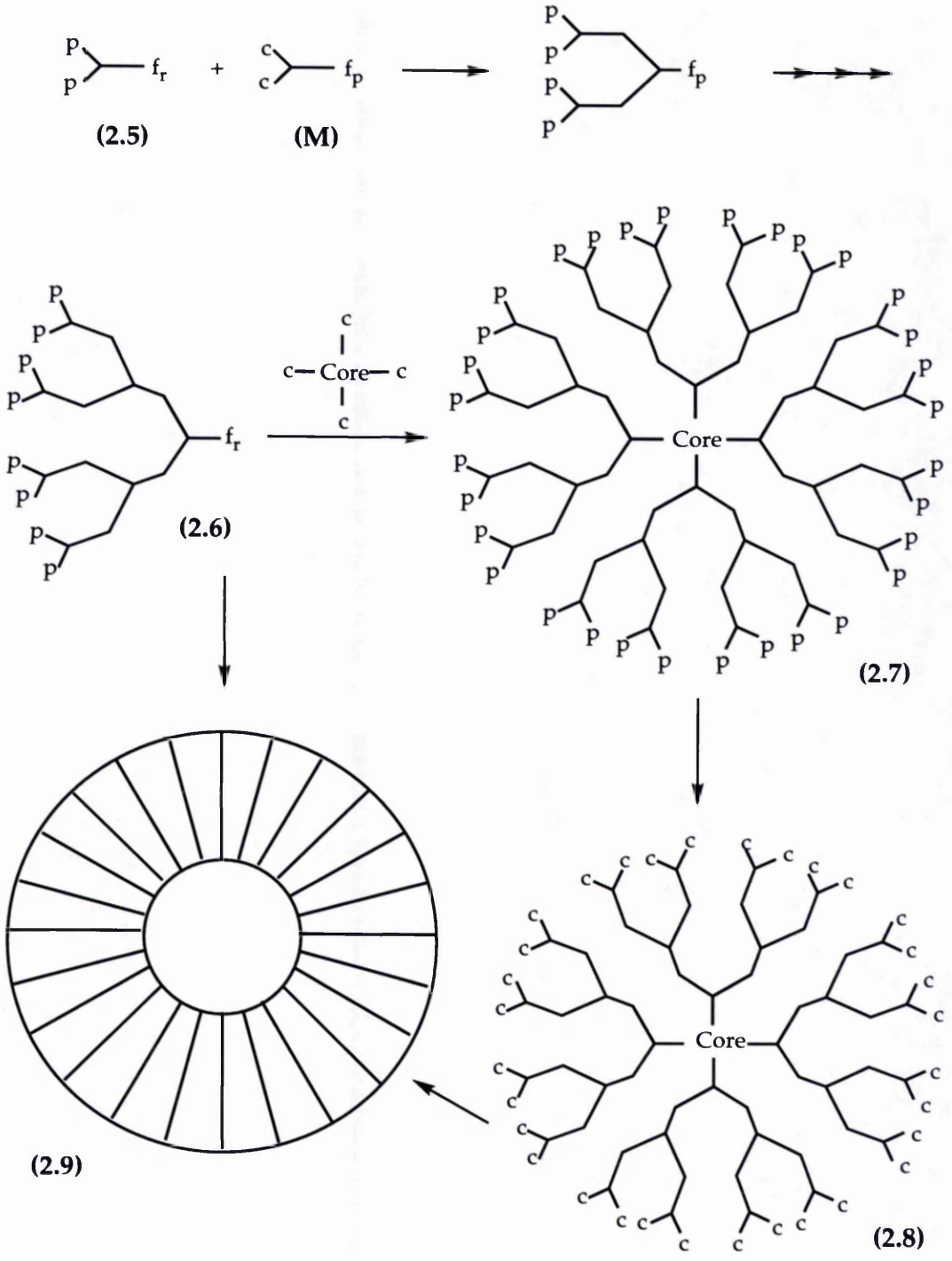
Scheme 2.1 Fréchets *'convergent growth'* approach to dendrimer synthesis.

The synthesis of sixth generation dendritic fragments have been reported using this methodology[6] although other groups have found difficulty in reproducing the excellent reported yields.[9] Although C-alkylation of phenols is a well known side reaction,[10] no evidence of C-alkylation was observed in the reaction products by ^{1}H and ^{13}C NMR spectra for any generation. By employing a high polarity solvent (acetone) and the crown ether to complex the potassium ion, it is possible to reduce C-alkylation by affording the more reactive 'naked' phenoxide ion thus promoting O-alkylation.

2.1.3 Synthesis of Dendrimer Fragments based on 4,4-bis(4'(hydroxy) phenyl) pent-1-ol

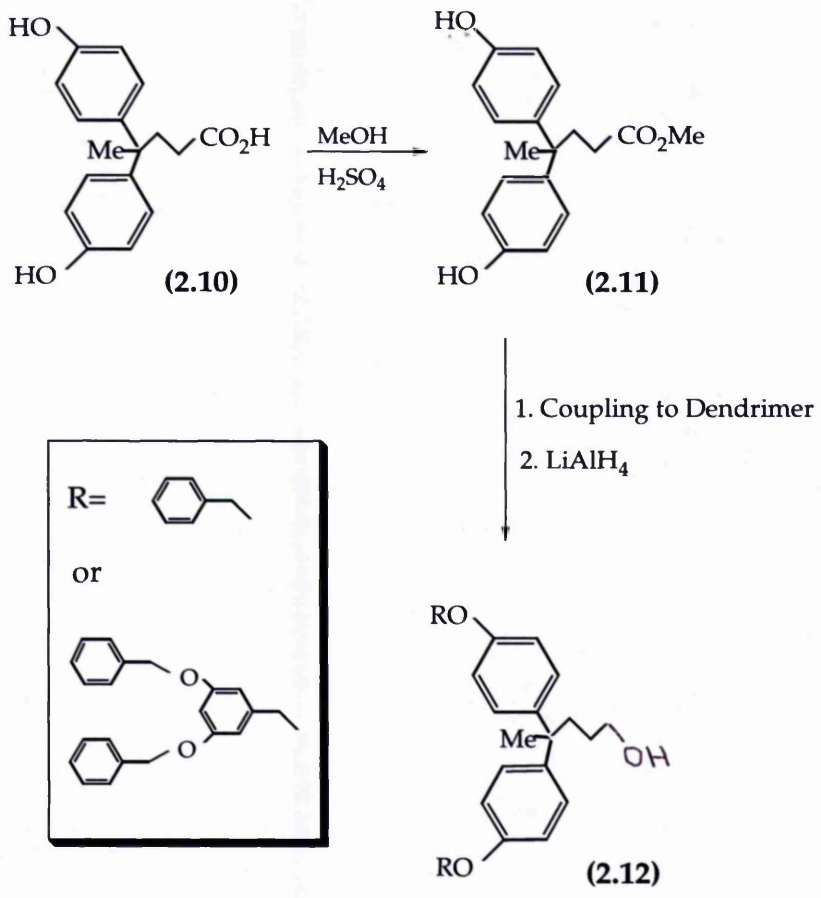
A particular feature of the convergent-growth technique is that the inner hyperbranched core *'hypercore'* may be constituted of flexible segments. Coupling of the dendritic fragments to this loose hypercore reduces the steric constraints encountered on attachment of the dendritic wedges to the central core unit[7] (Scheme 2.2).

The first stage of this approach is the preparation of the flexible hypercore moiety. The synthesis starts at what will become the periphery of the hypercore, through coupling of the protected surface moiety (**2.5**) which contains at least two protected functional groups (p) and one reactive functional group (f_r), with a monomer unit (**M**), which has at least two coupling sites (c) and a protected functional group (f_p). Repetition of the previously described[6, 7] convergent strategy leads to dendritic fragments such as (**2.6**).



Scheme 2.2

Coupling of (**2.6**), which contains a single reactive functional group (fr) and a large number of surface groups (p), to a *normal* core molecule would give the dendritic fragment (**2.7**), which as shown (Scheme 2.2) has 32 protected peripheral groups. Deprotection of these groups gives the desired hyperfunctionalised core molecule (**2.8**), which contains 32 coupling sites (c). The second stage of this approach involves reaction of a dendritic fragment such as (**2.6**) with the hypercore (**2.8**) to give the hyperbranched macromolecule (**2.9**). This is shown schematically in two dimensions showing the dendritic fragments as wedges attached to the central hypercore.



Scheme 2.3

The monomer unit for the initial convergent preparation of the hypercores (**2.12**) was chosen because of its increased flexibility. Substitution of the phenolic groups with either benzyl alcohol or [G-1]-OH was performed before reduction to give the desired monomer. Monomer (**2.12**) was prepared as shown in Scheme 2.3.

Esterification of the commercially available acid (**2.10**) with methanol/H_2SO_4 afforded the methyl ester (**2.11**). Subsequent Williamson coupling of (**2.11**) with benzyl chloride in DMF followed by reduction of the ester functionality with lithium aluminium hydride afforded (**2.13**). Whilst DCCI[11] coupling of (**2.11**) with [G-1]-OH, again followed by ester reduction yielded (**2.14**) (Fig. 2.1).

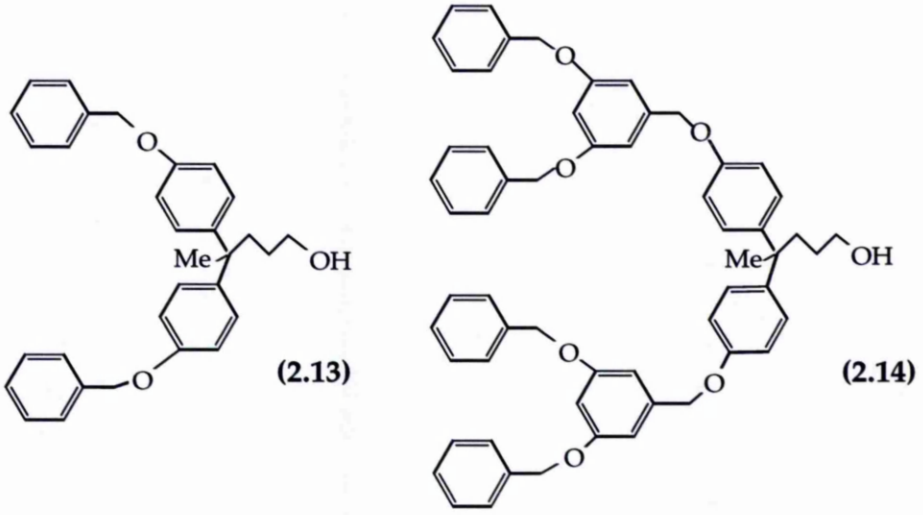
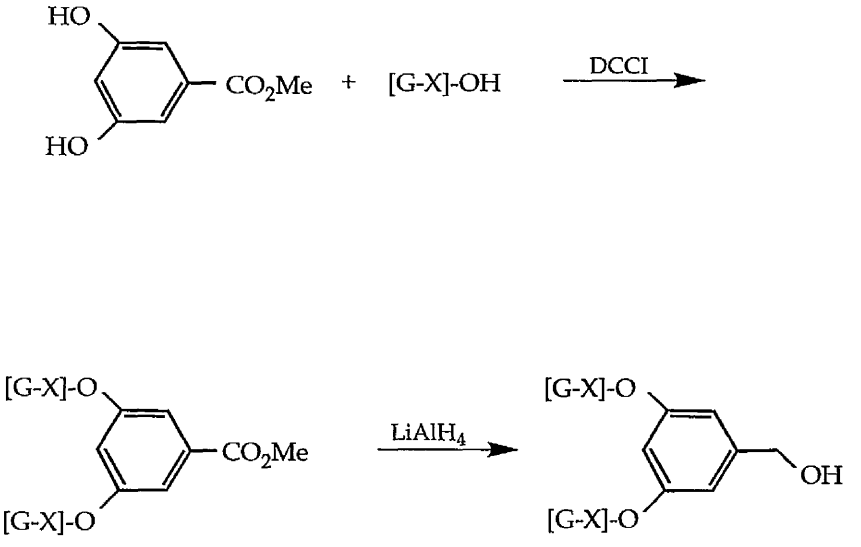


Fig. 2.1

2.1.4 Synthesis of Dendrimers via an "Alternative Convergent" Approach

Due to the synthesis of aryl ether dendrimers by the reported methods[6] producing only modest yields of materials, an alternative synthesis was employed, similar to that used in the synthesis of the dendrimers based on 4,4-bis(4'-hydroxyphenyl) pent-1-ol (Scheme 2.4).

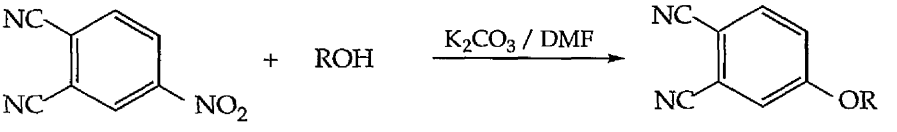
Methyl 3,5-dihydroxy benzoate was prepared from the reaction between the commercially available 3,5-dihydroxy benzoic acid and sulphuric acid in methanol. Coupling of the appropriate dendrimer fragment was achieved using DCCI[11] and the dendritic alcohol, followed by reduction of the methyl ester using lithium aluminium hydride to yield the respective next generation alcohol. This method proved successful for producing large quantities of [G-2]-OH and [G-3]-OH, but unsuccessful for any higher generations.



Scheme 2.4

2.2 Synthesis of Mono Substituted Dendritic Phthalonitrile Precursors

The precursor dendritic phthalonitriles were prepared by the SNAr reaction of 4-nitrophthalonitrile with an appropriate dendritic alcohol (Scheme 2.5), using a dipolar aprotic solvent such as dimethylformamide. This type of reaction has proved successful in providing a large number of substituted phthalonitriles.[12]

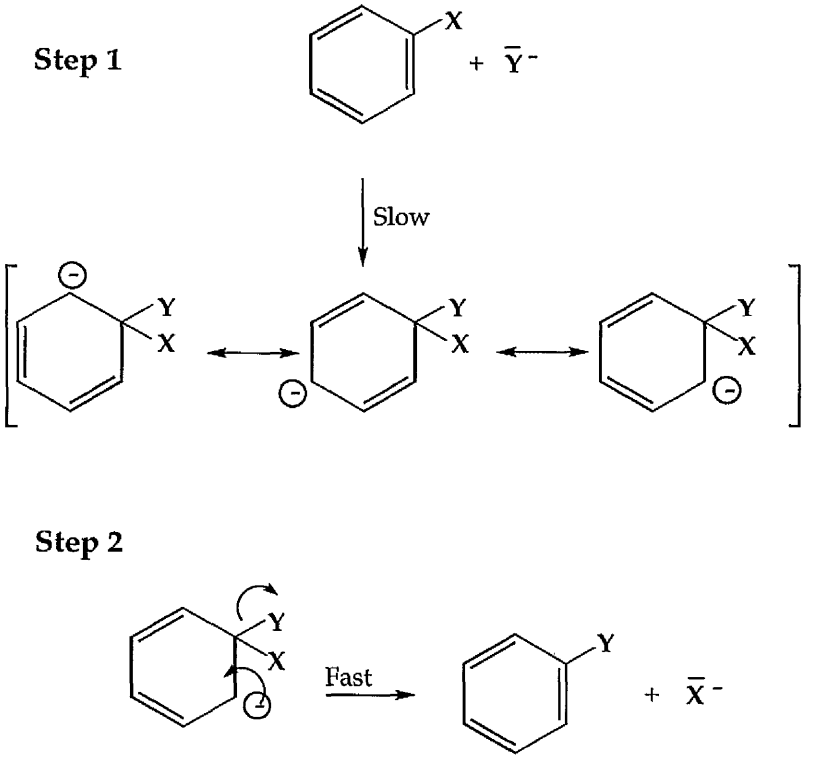


Scheme 2.5

Most nucleophilic aromatic substitution reactions occur via the two step S_NAr mechanism, with the primary step usually rate determining, (Scheme 2.6). These substitutions are accelerated by electron withdrawing groups, especially in the positions *ortho* and *para* to the leaving group.[13] The activating group stabilises the intermediates, and the transition states leading to them, by withdrawing electron density, thus accelerating the reaction rate.

Elimination of the more stable nucleofuge then occurs (Step 2). Thus a nitro group will aid the ease of S_NAr displacements at the *ortho* and *para* positions. In the case of 4-nitrophthalonitrile, where the aromatic ring is activated with more than one electron-withdrawing substituent, substitution of the nitro, rather than the cyano moiety occurs due to the higher nucleofugicity of the nitro group.

The nucleophiles used in the synthesis of mono substituted dendritic phthalonitriles, were formed by the deprotonation of the appropriate dendritic or benzylic alcohol using potassium carbonate in DMF. This then provided the attacking species RO^- for nucleophilic aromatic substitution and the formation of the required precursor.

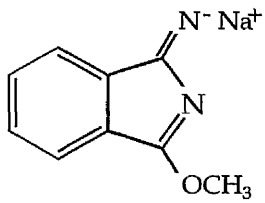


Scheme 2.6

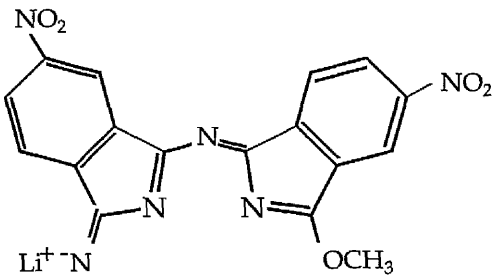
2.3 Cyclotetramerisation of Phthalonitrile Precursors

The precise mechanisms of the various phthalocyanine formation reactions is not known. However, the reaction of alkali metal alkoxides with phthalonitrile has been studied and intermediates such as (**2.15**) [14, 15] and (**2.16**) [16] isolated (Fig. 2.2). It can be assumed that

nucleophilic attack of the alkoxide on the carbon of a nitrile group occurs, followed by ring closure to form the isoindole derivative (**2.15**). The negatively charged imine nitrogen can then act as the nucleophile to attack another nitrile and form a dimer (**2.16**). With a further two additions of this type the skeleton of the phthalocyanine ring could be formed. However, reduction involving the addition of two hydrogen atoms is required to complete the aromatic ring structure, it is however, not certain when this occurs.



(2.15)



(2.16)

Fig. 2.2

Most of the phthalocyanines described were synthesised using a refluxing solution of lithium metal dissolved in pentanol (lithium pentoxide) to form Li_2Pc, which can be readily demetallated using dilute aqueous acid.

2.4 Synthesis of Metal-Free *2, 9(10), 16(17), 23(24)*-Tetra-Substituted Phthalocyanines from Novel Phthalonitrile Precursors.

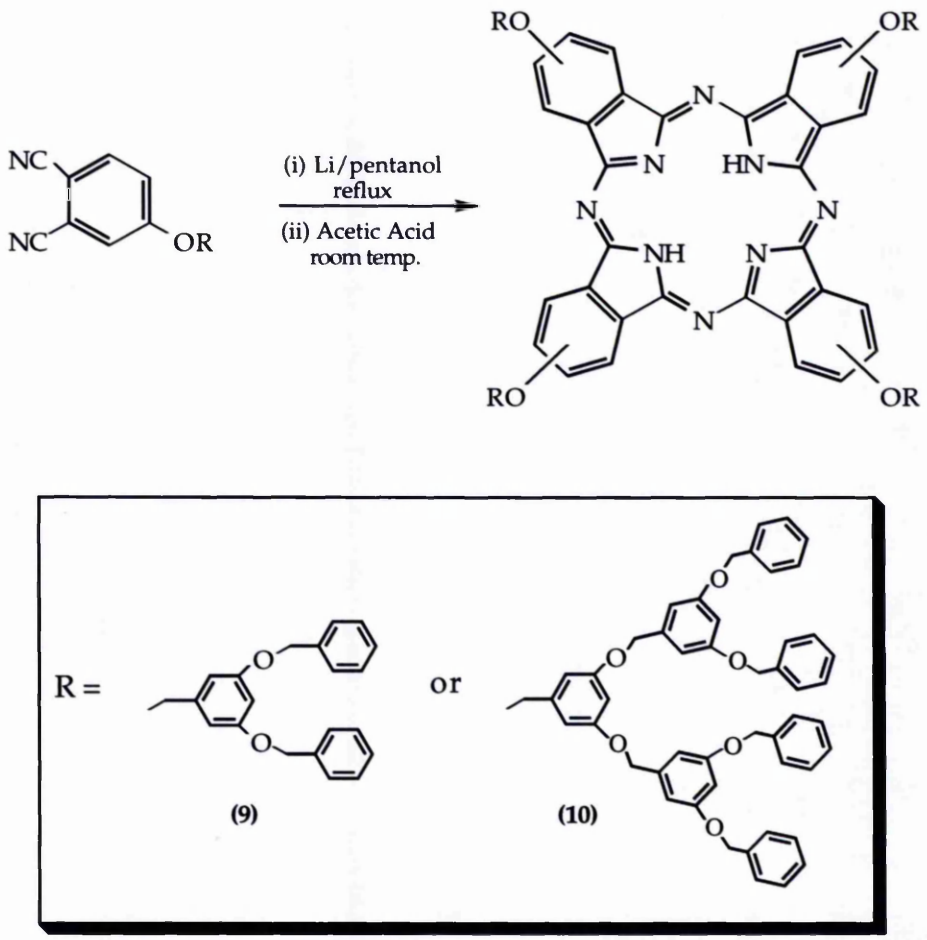
2.4.1 Synthesis of Tetra Substituted Phthalocyanines with Aryl Ether Dendrimers (9), (10), (11)

The precursors 4-[G-1] phthalonitrile, [G-1]-Pn **(1)**, 4-[G-2] phthalonitrile, [G-2]-Pn **(2)** and 4-[G-3] phthalonitrile, [G-3]-Pn **(3)**, were synthesised by the nucleophilic substitution of the appropriate dendritic alcohol with 4-nitrophthalonitrile (Scheme 2.5). Yields were 90 % for [G-1]-Pn **(1)**, 85 % for [G-2]-Pn **(2)** and 79 % for [G-3]-Pn **(3)**.

Metal free 2, 9,(10), 16,(17), 23,(24)-tetra [G-X] phthalocyanines **(9), (10), (11)**, were prepared by the lithium pentyloxide cyclotetramerisation of 4-[G-X] phthalonitrile **(1), (2), (3)**, in refluxing pentanol (i), followed by addition of 95 % acetic acid (0.5 ml) (ii), to afford the metal free phthalocyanines as a mixture of inseparable isomers (Scheme 2.7). Due to initial difficulties in forming [G-2]-Pc **(10)** and [G-3]-Pc **(11)** using the lithium pentoxide mediated process a number of other cyclotetramerisation methods were attempted but without significant improvements, (see experimental chapter) and the desired materials were eventually prepared by the usual lithium/pentanol route.

Purification of 2, 9,(10), 16,(17), 23,(24)-tetra-[G-X] phthalocyanines **(9), (10), (11)**, was achieved in each case by column chromatography or preparative TLC and the yields of pure isolated product were between 10-18 %.

UV/Vis spectroscopy of these phthalocyanines showed the characteristic split Q-band of a non-aggregated metal free-phthalocyanine at 718 nm and 682 nm. The δ_H NMR, IR, FAB mass spec. (if appropriate) and elemental analysis were all consistent with the expected structures.

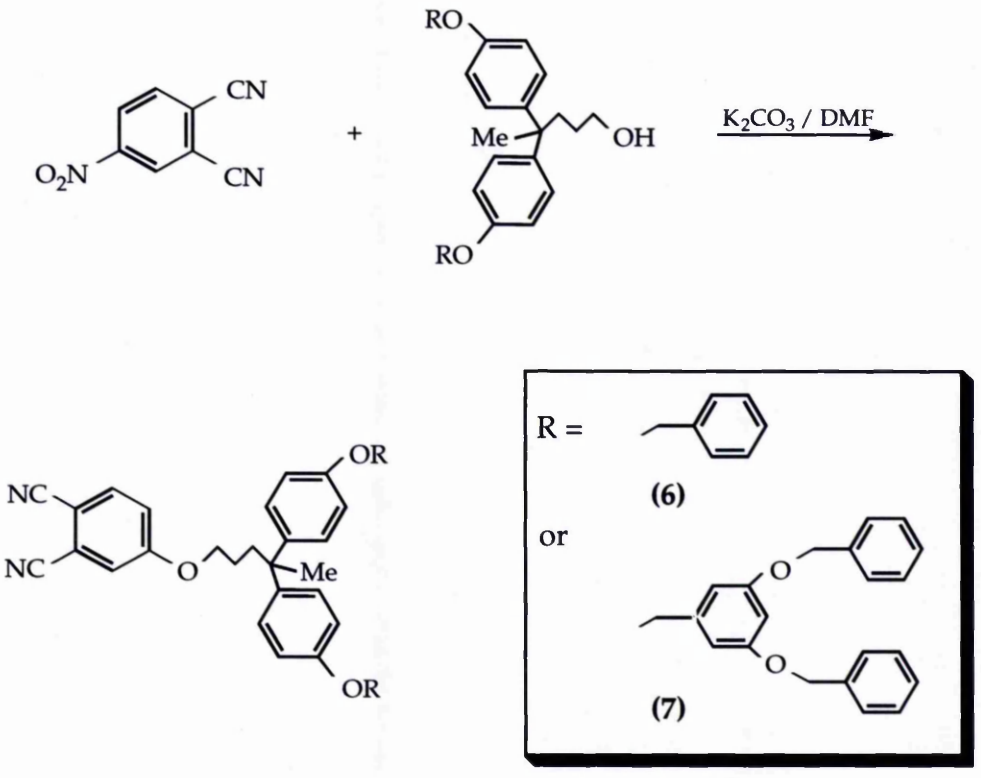


Scheme 2.7

Using similar synthetic methodology metal free 2, 9,(10), 16,(17), 23,(24)-tetra [G-1] and [G-2] phthalocyanines in which an ethylene spacer is placed between the dendritic substituents and the Pc core were prepared **(12), (13)** and analysed as for the benzyl ether phthalocyanines **(9), (10), (11)**. All were shown to be consistent with the expected structures and the yields of the pure isolated product were 40 % for the 4-(2'-(3",5"-dibenzyloxy)benzyloxyethyloxy) phthalocyanine **(12)** and 37 % for 4-(2'-(3",5"-di(3"',5"'-dibenzyloxy)benzyloxy)benzyloxyethyloxy) phthalocyanine **(13)**.

2.4.2 Synthesis of Tetra Substituted Phthalocyanines with Dendritic Substituents based on 4,4-bis[4'(hydroxy)phenyl] pent-1-ol (14)

The 4-(4',4'-bis(4"-benzyloxyphenyl)pentyloxy) phthalonitrile **(6)** was prepared, in 73 % yield, using the same procedures as for the benzyl ether linked phthalonitriles (Scheme 2.8). The synthesis of the analogous dendroxy phthalonitrile 4-bis(4'-(3",5"-dibenzyloxy)benzyloxyphenyl) phthalonitrile **(7)** was attempted but failed. From the resulting NMR and FAB mass spectra, the only products were 4-nitrophthalonitrile and the starting alcohol. The preparation of 2, 9,(10), 16,(17), 23,(24)-tetra (4',4'-bis(4"-benzyloxyphenyl)pentyloxy) phthalocyanine **(14)** was carried out using the lithium pentyloxide catalysed cyclotetramerisation of phthalonitrile **(6)** in refluxing pentanol to yield the metal-free phthalocyanine in 9 % yield as a mixture of inseparable isomers.



Scheme 2.8

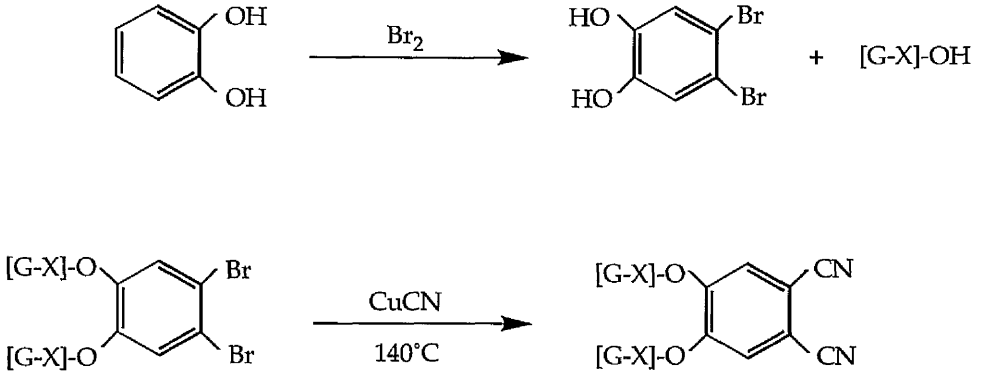
2.4.3 Synthesis of Tetra Substituted Naphthalocyanine (15)

The precursor 6-(3',5'-dibenzyloxybenzyloxy)-2,3-naphthalonitrile ([G-1]-NPn) **(8)** was also synthesised, by the DCCI coupling[11] of [G-1]-OH and 6-(hydroxy)-2,3-naphthalonitrile, kindly donated by Mr. Matthew Brewis. Yield of pure product was 50.3 %. The tetra-[G-1]-naphthalocyanine **(15)** was synthesised from the phthalonitrile precursor **(8)** by the usual lithium pentyloxide cyclotetramerisation. This was also analysed as for the benzyl ether phthalocyanines **(9), (10), (11)**. The product was shown to be consistent with the expected structure although the δ_H 500 MHz NMR was featureless and inconclusive. The yield of the pure isolated product was 4.5 %.

2.5 Synthesis of *2,3,9,10,16,17,23,24*-Octa-Substituted Phthalocyanines

2.5.1 Synthesis of *2,3,9,10,16,17,23,24*-Octa-Substituted Phthalocyanines with Aryl Ether Dendritic substituents (28), (29)

Bromination of catechol afforded 4,5-dibromo-1,2-dihydroxybenzene on which DCCI coupling[11] of the appropriate dendritic alcohol was then performed.[17] Conversion of the 4,5-dibromide to the phthalonitrile was accomplished by refluxing with copper(I)cyanide in DMF.[18, 19, 20] The precursors 4,5-bis(3',5'-dibenzyloxy)benzyloxy phthalonitrile **(21)** and 4,5-bis(3',5'-di(3'',5''-dibenzyloxy)benzyloxy)benzyloxy phthalonitrile **(22)** were prepared in 22 % and 3 % yield respectively, based on the original amount of dibromocatechol used. The [G-3] analogue could not be prepared, presumably due to the steric constraints encountered with the ortho substitution (Scheme 2.9).



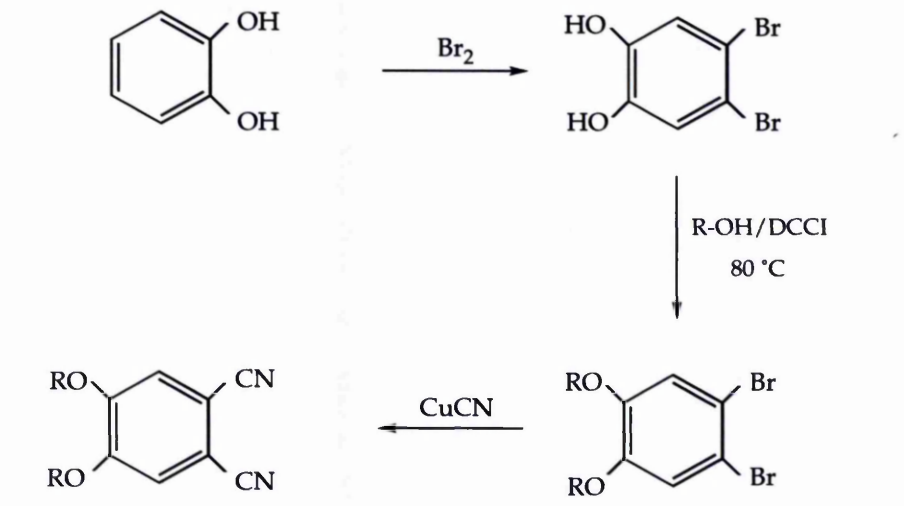
Scheme 2.9

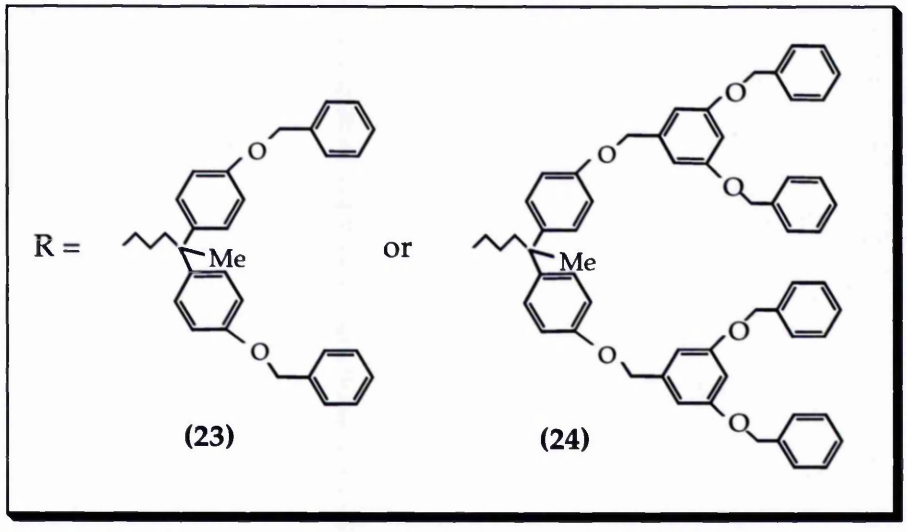
Metal free 2, 3, 9, 10, 16, 17, 23, 24-octa [G-1] phthalocyanine **(28)**, was prepared by the lithium pentyloxide catalysed cyclotetramerisation of 4,5-bis(3',5'-dibenzyloxy)benzyloxy phthalonitrile **(21)** in refluxing pentanol (i), followed by addition of 95 % glacial acetic acid (0.5 ml) (ii), to afford the crude metal-free phthalocyanine. Purification was achieved by column chromatography and yields of pure isolated product was 17 %.

Similarly, the synthesis of metal free 2, 3, 9, 10, 16, 17, 23, 24-octa [G-2] phthalocyanine **(29)** was attempted, however, spectroscopic analysis of the resultant materials failed to confirm the expected structure.

2.5.2 Synthesis of Octa Substituted Phthalocyanines with Dendritic Substituents based on 4,4-bis(4'(hydroxy)phenyl) pent-1-ol (31), (32)

4,5-bis(4',4'-bis(4''-benzyloxyphenyl)pentyloxy) phthalonitrile **(23)** and the analogous [G-1] dendroxy phthalonitrile 4,5-(4',4'-bis(4''-(3''',5'''-dibenzyloxy)benzyloxyphenyl)pentyloxy) phthalonitrile **(24)** were prepared as for the 4,5-diaryl ether phthalonitriles **(21)** and **(22)** (Scheme 2.9) in 71 % and 76 % yield respectively. Metal free 2, 3, 9, 10, 16, 17, 23, 24-octa-(4',4'-bis(4''-benzyloxyphenyl)pentyloxy) phthalocyanine **(31)**, was prepared by lithium pentyloxide catalysed cyclotetramerisation of 4,5-bis(4',4'-bis(4''-benzyloxyphenyl)pentyloxy) phthalonitrile **(23)** (Scheme 2.10). Purification was achieved by column chromatography and yields of pure isolated product were 3 %.





Scheme 2.10

The δ_H NMR (500 MHz at 60 °C), IR (KBr disc), FAB mass spectra and elemental analysis all proved consistent with the expected structure. The UV/Vis in toluene showed the characteristic split Q-band of a non-aggregated metal-free phthalocyanine. The cyclotetramerisation of the analogous dendroxy phthalonitrile 4,5-(4',4'-bis(4''-(3''',5'''-dibenzyloxy)benzyloxyphenyl)pentyloxy) phthalonitrile **(24)** was also attempted but failed to produce any phthalocyanine.

2.6 Synthesis of Asymmetrically Substituted Phthalocyanines Bearing a Single Dendritic Fragment

Non-uniformly substituted phthalocyanines can be prepared by mixed phthalonitrile cyclotetramerisations, although complex phthalocyanine product mixtures are obtained, which require separation by column chromatography of silica. However by using one phthalonitrile in great excess it is possible to obtain a product mixture which is essentially composed of only two Pcs[21, 22, 23, 24]

Recent work within this research group has shown that the combined use of oligo(ethyleneoxy) phthalonitriles and phthalonitriles with alkyl substituents at the 4,5 positions allows excellent separation of complex phthalocyanine mixtures including *opposite* and *adjacent* regioisomers, by the use of simple column chromatography.[21] Generally the number of polar oligo(ethyleneoxy) side-chains attached to the phthalocyanine, the longer it is retained on the column. Therefore, it was predicted that a mixed phthalocyanine reaction between dendroxy phthalonitriles and an excess of 4,5-(1,4,7-trioxaoctyl) phthalonitrile (Fig. 2.3) would allow formation of a product mixture from which individual Pc materials could be isolated.

The main interest focused on the synthesis of phthalocyanines containing only one dendroxy subunit and six 1,4,7-trioxaoctyl side-chains. This AB_3 phthalocyanine proved to be easily separated from any trace A_2B_2 phthalocyanine by column chromatography and was expected to yield interesting information on the effect of the size of the dendritic substituent

on the ability of the Pc subunit to induce columnar liquid crystallinity.

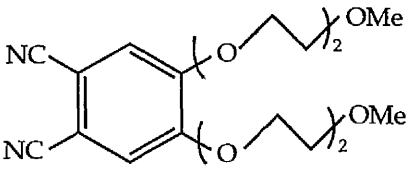


Fig. 2.3

Thus, a series of phthalocyanines substituted in this way were prepared with 1,2-(1,4,7-trioxaoctyl) phthalonitrile and [G-1]-phthalonitrile **(1)**, [G-2]-phthalonitrile **(2)** and [G-3]-phthalonitrile **(3)**. Each of the isolated phthalocyanines gave elemental analyses, UV/vis absorption spectra, δ_H NMR spectra and fast atom bombardment (FAB) mass spectra consistent with their proposed structures. The phthalocyanines were synthesised in 51 % yield for 2-(3',5'-dibenzyloxy)benzyloxy-9,10,16,17,23,24-hexa(1,4,7-trioxaoctyl) phthalocyanine **(33)**, 33 % yield for 2-((3',5'-di(3",5"-dibenzyloxy)benzyloxy)benzyloxy)-9,10,16,17,23,24-hexa(1,4,7-trioxaoctyl) phthalocyanine **(35)** and 9 % yield for 2-((3',5'-di(3",5"-di(3"',5"'benzyloxy)benzyloxy)benzyloxy)benzyloxy)-9,10,16,17,23,24-hexa(1,4,7-trioxaoctyl)phthalocyanine **(37)**, respectively based on the mass of phthalonitrile used.

Similarly, the synthesis of phthalocyanines containing three 1,2-(1,4,7-trioxaoctyl) subunits and one 4,5-substituted phthalonitrile subunit were prepared with 4,5-bis(3',5'-dibenzyloxy)benzyloxy phthalonitrile **(21)** and 4,5-bis(3',5'-di(3",5"-dibenzyloxy)benzyloxy)benzyloxy phthalonitrile **(22)**. Surprisingly, the NMR spectra for the resulting phthalocyanine compound **(34)** showed evidence of the Ha proton (Fig 2.4) being present (see also Fig. 3.2). This suggests that the dendritic fragment was

reductively cleaved during the cyclotetramerisation reaction and is consistent with peaks in the mass spectra of both Pcs **(34)** and **(36)**, corresponding to parent ion of the mono dendroxy substituted product. From the FAB mass spec. there seems to be equal amounts of the mono and di-substituted dendritic phthalocyanines present. Further evidence for the reductive cleavage is seen in the elemental analyses, which give values between those expected for the mono and di dendrimer substituted product. The mixtures of phthalocyanines were synthesised in good yield, 20 % for the 2,3-di((3',5'-dibenzyloxy)benzyloxy)-9,10,16,17,23,24-hexa(1,4,7-trioxaoctyl) phthalocyanine **(34)** and 43 % for 2,3-bis((3',5'-di(3'',5''-dibenzyloxy)benzyloxy)benzyloxy)-9,10,16,17,23,24-hexa(1,4,7-trioxaoctyl) phthalocyanine **(36)**.

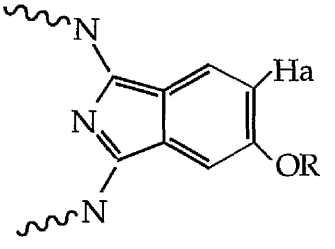


Fig 2.4

2.7 Alternative methods of Phthalocyanine Formation

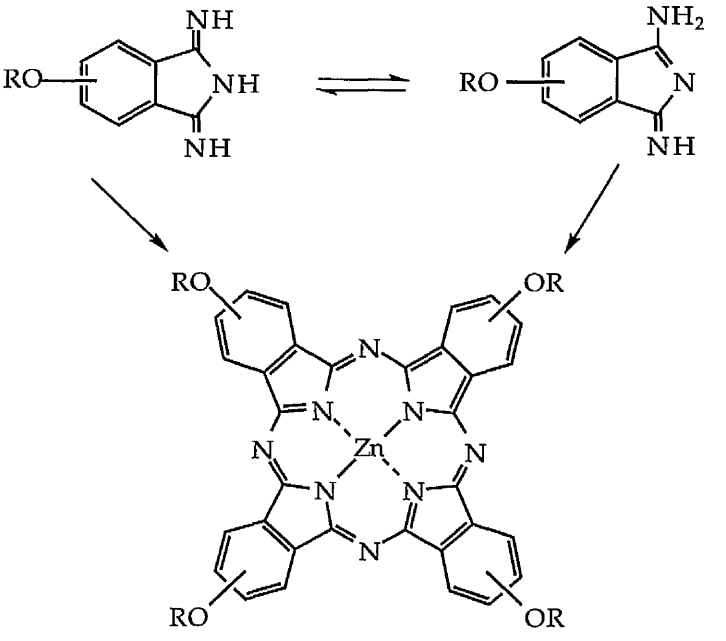
2.7.1 Zinc Templating (i)

The basic macrocycle was synthesised by condensation of 4-substituted [G-1] and [G-2] phthalonitriles with zinc(II)acetate dihydrate at 200°C.[25] The Zn acts as a Lewis acid and nitrogen of the nitrile group as a Lewis

base thus increasing the chances of the phthalonitrile units coming together for the cyclotetramerisation reaction. The tetra [G-1] substituted Zn-Pc **(38)** was obtained as a dark blue solid in good yield and gave the characteristic UV/vis spectrum of a metal containing phthalocyanine. The expected structure was further confirmed by δ_H 500 MHz NMR at 60 °C, IR (KBr disc) and elemental analysis. MS (FAB) showed the presence of the molecular ion. However, for the tetra [G-2] Zn-Pc **(40)**, IR (KBr disc), elemental analysis, UV/vis (toluene), δ_H NMR (500 MHz, $CDCl_3$ at 60 °C) and MS (FAB) all proved inconclusive. The synthesis was also attempted with 4-substituted [G-1] phthalonitrile and copper(II)acetate. Although some dark blue product was obtained δ_H 500 MHz NMR at 60 °C, IR, elemental analysis and MS (FAB) all proved inconclusive.

2.7.2 Zinc Templating (ii)[26]

[G-1] phthalonitrile was reacted at 100 °C with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a base, and zinc acetate as a template during which time ammonia gas was introduced into the solution to promote the formation of diiminoisoindoline, and the formation of the resultant phthalocyanine **(41)** (Scheme 2.11). However, after 10 hours at 100 - 115 °C, there was no detectable phthalocyanine formed.



Scheme 2.11

2.8 Substitution of Dendroxy Fragments onto Preformed Phthalocyanine Cores

2.8.1 Peripheral substitution

Substitution of dendritic fragments onto tetra-(3,5 di-tertiary-butyl-4-hydroxyphenyl) phthalocyanine, which was kindly provided by Mr. Paul Humberstone, was attempted. This worked well with [G-1]-Br to produce [G-1] substituted (3,5 di-tertiary butyl-4-hydroxyphenyl) phthalocyanine **(42)** in 34 % yield, but failed for high generations (see sections 4.12.5 and 4.12.6).

2.8.2 Axial substitution

The attractive possibility of using peripheral dendritic substituents to prevent cofacial aggregation in the solid phase was not realised (see discussion chapter). Higher generation dendritic substituents may be more successful but at the expense of diluting the effect of the functional Pc core. It was envisaged that axial substitution of silicon(IV) phthalocyanine with dendritic moieties would completely prohibit cofacial association although effects due to 'edge-to-edge' interactions may be observed. Attachment of [G-1], [G-2] and [G-3] dendritic wedges onto the phthalocyanine core was achieved by the reaction of the benzyl alcohol functionality with silicon phthalocyanine dichloride in the presence of sodium hydride. Due to the higher bond energy of a Si-O bond (466 kJmol -1) compared with Si-Cl (386 kJmol -1), displacement of the Cl with alkoxy nucleophiles occurs. This affords the axially substituted phthalocyanine with the dendrimer above and below the ring (Fig. 2.5). The resultant axially substituted [G-1] **(44)**, [G-2] **(45)** and [G-3] **(46)** phthalocyaninato silicons were purified by column chromatography and isolated in 14 %, 45 % and 18 % respectively. In each case they gave elemental analyses, δ_H NMR spectra and UV/vis spectra in correlation with their proposed structures (see discussion in sections 3.1.1 and 3.1.2). In addition, the structure of $[G\text{-}2]_2SiPc$ **(45)** was confirmed by a successful single crystal X-ray diffraction study (see section 3.2 and appendix 1).

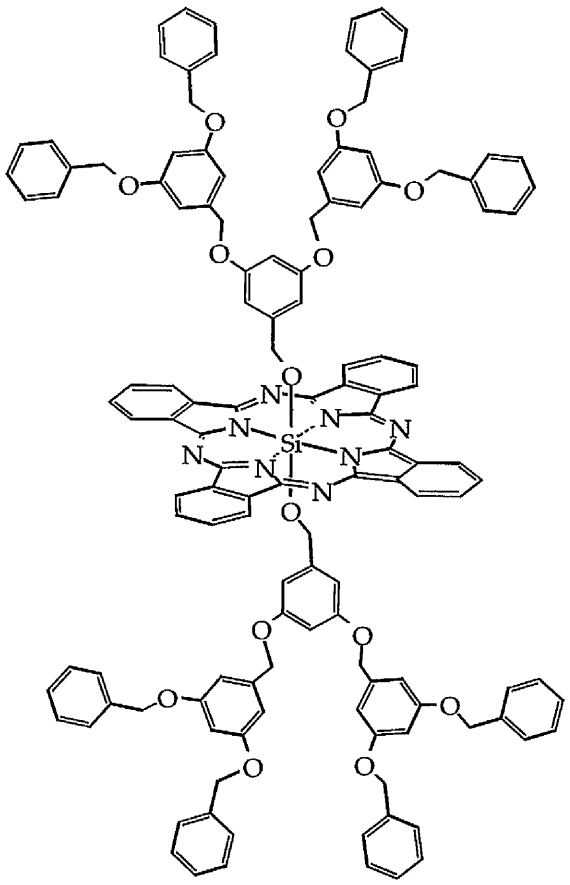


Fig. 2.5 The structure of $[G\text{-}2]_2SiPc$.

2.9 Chapter 2 References

1. Tomalia, D. A., Baker, H., Dewald, J., Hall, M., Kallos, G., Martin, S., Roeck, J., Ryder, J., Smith, P., *Polym. J.*, 1985, 17, 117

2. Tomalia, D. A., Baker, H., Dewald, J., Hall, M., Kallos, G., Martin, S., Roeck, J., Ryder, J., Smith, P., *Macromolecules*, 1986, 19, 2466

3. Newkome, G. R., Yao. Z., Baker, G. R., Gupta, V. K., *J. Org. Chem.* 1985, 50, 2004

4. Newkome, G. R., Baker, G. R., Saunders, M. J., Russo, P. S., Gupta, V. K., Yao, Z., Bouillion, J. E., *J. Chem. Soc., Chem. Commun.*, 1986, 752

5. Newkome, G. R., Yao, Z., Baker, G. R., Gupta, V. K., Russo, P. S., Saunders, M. J., *J. Am. Chem. Soc.* 1986, 108, 849

6. Hawker, C. J., Fréchet, J. M. J., *J. Am. Chem. Soc.*, 1990, 112, 7638-7647

7. Wooley, K. L, Hawker, C. J., Fréchet, J. M. J., *J. Am. Chem. Soc.*, 1991, 113, 4252-4261

8. Reimann, E., *Chem. Ber.*, 1969, 102, 2887

9. Personal communications Joachim Steinke

10. Kornblum, N., Seltzer, R., Haberfield, P. J., *J. Am. Chem. Soc.*, 1963, 85, 1148

11. Vowinkel, E., *Chem. Ber.*, 1966, 99, 62

12. Marcuccio, S. M., Svirskaya, P. I., Greenberg, S., Lever, A. B. P., Leznoff, C. C., Tomer, K. B., *Canadian Journal of Chemistry*, 1985, 63, 3057-69

13. Nurgatin, Sharnin, Ginzburg., *J. Org. Chem.*, USSR, 1983, 19, 343

14. Borodkin, V. F., *Zh. Prikl. Khim.*, 1958, 31, 813

15. *J. Appl. Chem. USSR*, 1958, 31, 813

16. Oliver, S. W., Smith, T. D., *J. Chem. Soc., Perkin Trans. 2.*, 1987, 1579

17. Kohn, M., *J. Am. Chem. Soc.*, 1951, 73, 480

18. Rappoport, Z., '*The Chemistry of the Cyano Group,*' Interscience Publishers, New York, 1970

19. Pawlowski, G., Hanack, M., *Synthesis*, 1980, 287

20. Friedman, L., Shechter, H., *J. Org. Chem.*, 1960, 26

21. Clarkson, G. J., McKeown, N. B., Treacher, K. E., *J. Chem. Soc. Perkin Trans. 1*, 1995, 1817

22. McKeown, N. B., Chambier, I., Cook, M. J., *J. Chem. Soc. Perkin Trans. 1*, 1990, 1169

23. Ikeda, Y., Konami, H., Hatano, M., Mochizuki, K., *Chem. Lett.*, 1992, 763

24. Limßen, T. G., Hanack, M., *Chem. Ber.*, 1994, 127, 2151

25. Kudrevich, S. V., Hasrat, A., van Lier, J. E., *J. Chem. Soc. Perkin Trans. 1*, 19, 1994

26. Leznoff, C. C., Mougang, H., McArthur, C. R., Qin, Y., *Can. J. Chem.* Vol. 72, 1994

3

Discussion

3.1 Spectrochemical and Chromatographic Analysis

3.1.1 δ_H NMR Investigations of the Series of Peripherally and Axially Substituted Pcs

So far, little has been said about the actual assignments of the claimed structures. δ_H NMR investigations are able to give such proof.

The general position of a signal in a nuclear magnetic resonance spectrum i.e. the strength of the magnetic field required to bring about the absorption of energy, can be related both to electron densities and aromatic ring currents in the compound. Generally, the greater the density of the electron cloud surrounding, or partially surrounding a proton, the more *upfield* is its chemical shift (a lower value of δ).

Electronegative groups (e.g. oxygen atoms) cause deshielding and this effect can be exerted *via* an aromatic ring. In addition, when an external magnetic field is imposed upon an aromatic ring (such as when the compound is placed in the magnetic field of a NMR spectrometer), the closed loop of aromatic electrons circulates in a diamagnetic ring current, which itself sends out a field. As can be seen in Fig. 3.1, this induced field curves around, and in the area of the peripheral protons, is parallel to the external field. Therefore, the field 'seen' by the aromatic protons is greater than it would have been in the absence of the diamagnetic ring current. The protons are moved *downfield* (to a higher value of δ), compared to where they would be if electron density were the only factor. For example, the aromatic protons of benzene derivatives are deshielded

because their locations are such that the induced magnetic field reinforces the applied magnetic field.

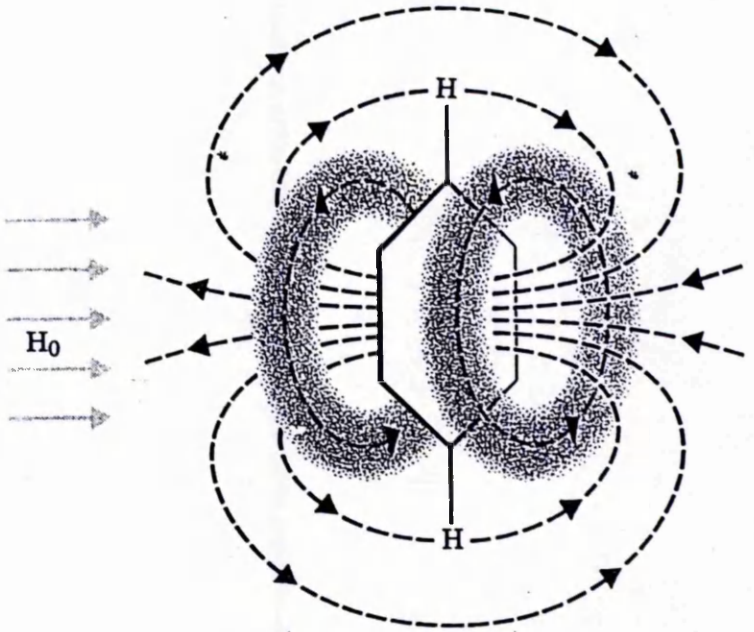


Fig. 3.1 Realms of Influence of the Aromatic Ring Current. The induced magnetic field of the π electrons of benzene dieshields the benzene protons. Deshielding occurs because at the location of the protons, the induced field is in the same direction as the applied field.

However, protons placed within the centre of a ring current, as in the case of the two internal protons of metal-free Pc, absorb at unusually high magnetic field strengths (-2.18 to -1.60 ppm), because they are highly shielded by the opposing induced field and hence, exhibit chemical shifts less than zero. In the case of the axially substituted Pcs **(44)**-**(46)** the protons in the dendritic wedges are located above and below the ring. These also have reduced chemical shifts relative to analogous protons of the same substituents placed at peripheral sites on Pcs **(33)**, **(35)** and **(37)**. From a comparison of the chemical shifts of the dendritic protons of Pcs **(33)**, **(35)** and **(37)** with those of Pcs **(44)**-**(46)** and using the shifts of the

analogous protons of [G-3]-OH as a standard (Tables 3.1 and 3.2), it is possible to show the influence of the Pc ring current at varying distances from the edge and centre of the macrocycle. In effect this analysis can 'map' out the magnetic field of the induced ring current.

Proton	[G-3]-OH	Pc (33)	Pc (35)	Pc (37)
a	4.57	5.54	5.53	5.50
b	6.42	7.05	7.03	7.00
c	6.36	6.69	6.65	6.49
d	4.94	5.18	5.10	5.06
e	6.48	-	6.73	6.72
f	6.36	-	6.60	6.48
g	4.94	-	4.98	4.98
h	6.50	-	-	6.69
i	6.39	-	-	6.52
j	5.00	-	-	4.88
k	7.27-7.41	7.22-7.50	7.18-7.32	7.15-7.35
l	-	8.55-8.70	8.52-8.70	8.52-8.72
m	-	9.05	9.02	9.05

Table 3.1 Chemical Shifts of the protons of Pcs **(33)**, **(35)** and **(37)** relative to [G-3]-OH from δ_H 500 MHz NMR spectra. This shows the effect of the ring current of the Pc macrocycle on proton chemical shift. (See Fig. 3.2 for key to proton lettering).

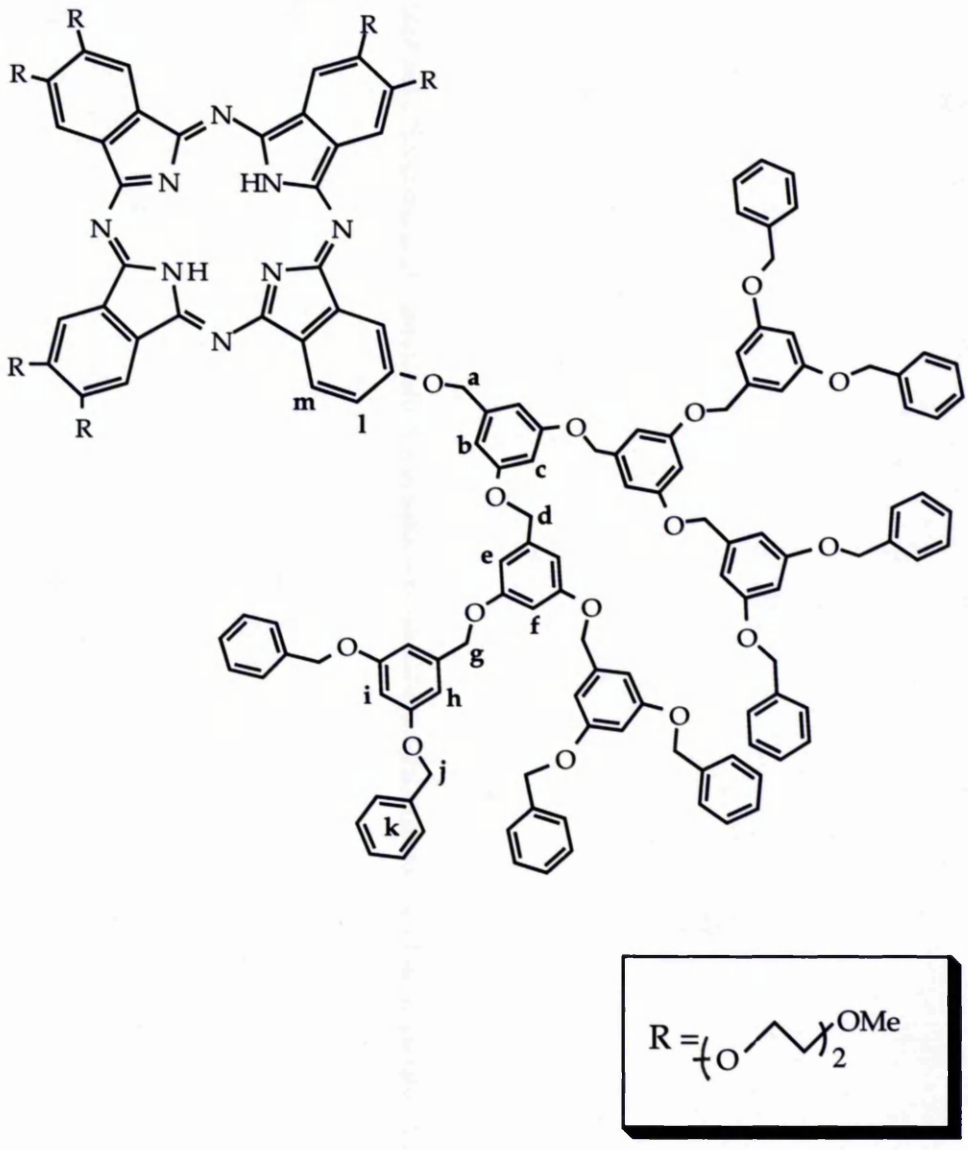


Fig. 3.2 [G-3] unsymmetrically substituted Phthalocyanine **(37)**. Letters indicate protons as referred to in Table 3.1

It can be seen from Table 3.1, that three main regions are apparent in the 500 MHz spectrum of [G-3]-OH. The resonances for the exterior phenyl protons **(k)**, occur at 7.27-7.41 ppm, the resonances for the aromatic protons of the monomer units **(b)**, **(c)**, **(e)**, **(f)** and **(h)**, **(i)** occur at 6.36-6.50 ppm, separate resonances can be seen for each 'layer' of monomer units. The signals due to the aromatic dendrimer protons also

give information on the number of protons giving rise to the signals and their positions on the benzyl ether. The protons, **(b)**, **(e)** and **(h)** appear as doublets due to their meta coupling (J = 2 Hz), with protons **(c)**, **(f)** and **(i)** respectively, and protons **(c)**, **(f)** and **(i)** appear as triplets due to their respective meta coupling with protons **(b)**, **(e)** and **(h)**. At the highest field, resonances for the benzylic protons **(a)**, **(d)** and **(g)** occur in the region 4.57-4.94 ppm. The benzylic protons **(a)** occur furthest upfield at 4.94 ppm, due to the electron withdrawing effect of the OH group.

In the case of the unsymmetrical Pcs **(33)**, **(35)** and **(37)**, the signals produced from protons on atoms within three bond lengths of the aromatic Pc ring are broadened due to aggregation, even though attempts were made to minimise aggregation by using d_6 benzene or $CDCl_3$, and an elevated temperature of 60 °C. The region of the spectra of the unsymmetrical phthalocyanines at 3.47 to 4.74 ppm are the peaks due to the 1,4,7-trioxaoctyl chains. Each proton on a CH_2 unit of the 1,4,7-trioxaoctyl chain is split into a triplet since it has two protons on the neighbouring CH_2 unit.

Peripheral attachment of the dendrimers to Pc causes the signals generated by the benzylic protons **(a)** to occur in the region ~5.50 ppm. This is a shift downfield of ~+1.0 ppm compared with the analogous protons in [G-3]-OH. This can be attributed to the deshielding effect of Pc ring current and the induced field generated, which reinforces the applied magnetic field. The deshielding effect of the Pc ring current is less apparent for the benzylic protons **(d)** and they are shifted downfield by only ~+0.1 to +0.2 ppm compared with [G-3]-OH. For the distant benzylic protons **(g)**, this effect is no longer significant. Interestingly, the remote

benzylic protons **(j)** are shifted upfield by -0.12 ppm . This may indicate that these protons spend more time, on average, in the shielding portion of the Pc ring current.

The resonances for the aromatic protons of the monomer units **(b)**, **(c)**, **(e)**, **(f)**, **(h)** and **(i)** occur in the region of 6.48-7.05 ppm. Again separate resonances are observed in the appropriate ratio for each 'layer' of monomer units and the splitting pattern can be explained in the same way as for [G-3]-OH. The aromatic protons **(b)**, feel the strong deshielding effect of the Pc ring current, and are shifted downfield by ~+0.6 ppm compared with [G-3]-OH. The same argument as for the benzylic protons can be used, as the first generation aromatic protons **(e)** are deshielded less, and shifted downfield by only ~+0.25 ppm, the second generation aromatic protons **(h)** are shifted downfield by only +0.19 ppm. The aromatic protons **(c)**, **(f)** and **(i)**, which are split by meta coupling into triplets, show a similar shift downfield in each Pc regardless of their distance from the Pc. In Pc **(33)** the shift is +0.33 ppm for **(c)**, for Pc **(35)** the shift is +0.29 ppm for **(c)** and +0.24 ppm for **(f)** and for Pc **(35)** the shift is +0.13 ppm for **(c)**, +0.12 ppm for **(f)** and +0.13 ppm for **(i)**. This reduction in the influence of the Pc ring current for the larger dendritic wedges may be due to the larger number of adjacent benzene rings whose own ring currents mask the full effect of that of the Pc.

The exterior phenyl protons **(k)** occur between 7.22 and 7.50 ppm in Pc **(33)** this is a much broader multiplet than that seen in [G-3]-OH, suggesting aggregation of the sample. In Pcs **(35)** and **(37)** the protons are slightly shielded and shifted upfield by ~-0.1 ppm compared with [G-3]-OH. The peripheral and non-peripheral protons on the Pc ring **(l)**

and **(m)** show the same chemical shift in all three Pcs.

Proton	[G-3]-OH	Pc (44)	Pc (45)	Pc (46)
a	4.57	-0.69	-0.69	-0.68
b	6.42	3.58	3.54	3.50
c	6.36	5.64	5.64	5.61
d	4.94	4.11	4.02	3.97
e	6.48	-	6.32	6.32
f	6.36	-	6.46	6.45
g	4.94	-	4.96	4.85-5.10
h	6.50	-	-	6.65
i	6.39	-	-	6.54
j	5.00	-	-	4.85-5.10
k	7.27-7.41	7.20-7.40	7.20-7.40	7.20-7.40
l	-	8.20-8.31	8.20-8.31	8.20-8.31
m	-	9.52-9.62	9.52-9.62	9.52-9.62

Table 3.2 Chemical Shifts of the protons of Pcs **(44)**, **(45)** and **(46)**, relative to [G-3]-OH from δ_H 500 MHz NMR spectra. This shows the effect of the ring current of the Pc macrocycle on proton chemical shift. (See Fig. 3.3 for key to proton lettering).

Attention has been drawn to the fact[1] that groups located above and below the ring in porphyrin-type compounds are subject to an amount of shielding which increases as the proximity of the group to the ring centre increases. For groups quite near to the centre the shielding is substantial.[2, 3]

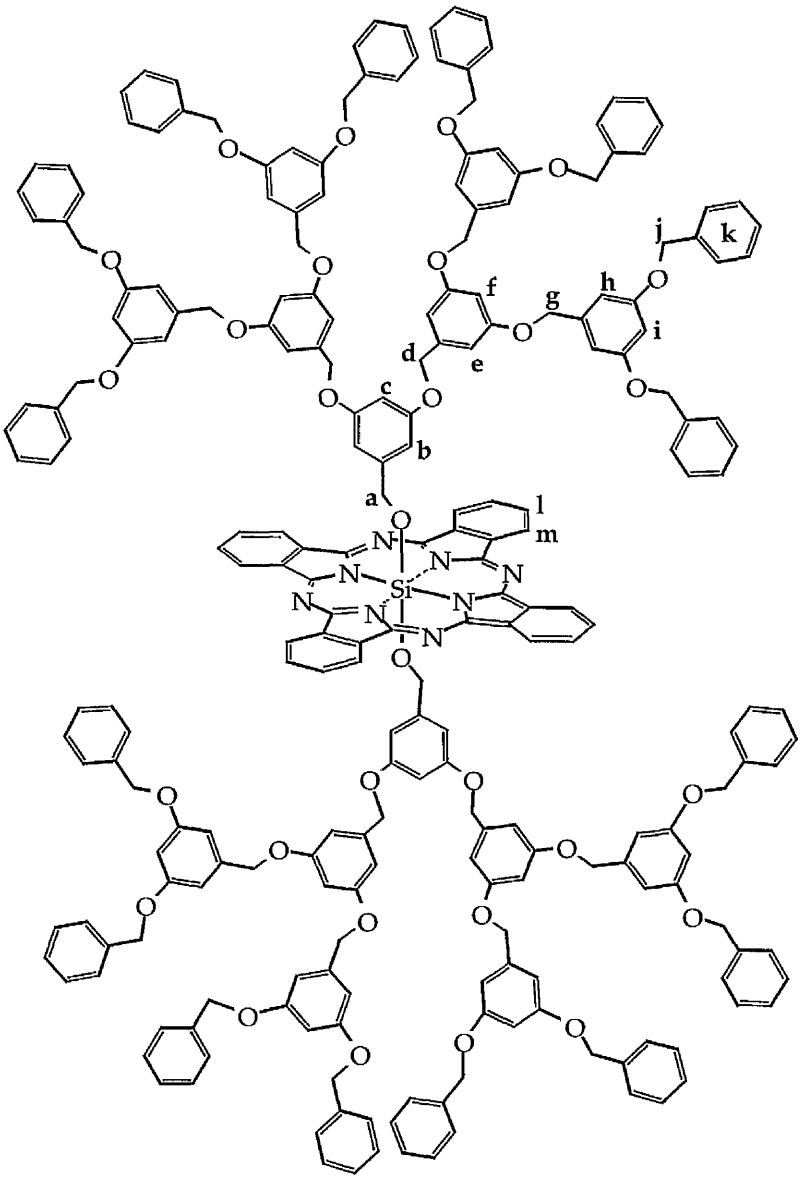


Fig. 3.3 [G-3]-axially substituted Phthalocyanine **(46)**. Letters indicate protons as referred to in Table 3.2.

This is beautifully illustrated by the spectra of Pcs **(44)**, **(45)** and **(46)**, the benzylic protons **(a)** are nearest to the Pc ring and are under the largest influence of the ring current. Indeed these protons occur at ~-0.69 ppm a shift of -5.25 compared with [G-3]-OH. This effect is reduced for the benzylic protons **(d)** which are shielded by only ~-1.0 ppm. The positions

of the benzylic protons **(g)** and **(j)** are largely unaffected by the ring current but they display splitting and broadening which may be due to the restricted motion on the NMR timescale of these remote moieties, resulting in different magnetic environments.

The resonances for the aromatic protons of the monomer units are much more shielded in the lower generation axially substituted Pcs. The aromatic protons **(b)**, feel the strong shielding effect of the Pc ring current and are shifted upfield by ~-2.9 ppm compared with [G-3]-OH. The protons **(e)**, are shielded less and shifted upfield by only -0.16 ppm in both Pcs **(45)** and **(46)**, and the remote protons **(h)**, are actually deshielded (+0.15 ppm) relative to the analogous protons on [G-3]-OH.

However the chemical shifts of the aromatic protons **(c)**, **(f)** and **(i)** are not easily explained. The aromatic protons **(c)** are once again shielded by the Pc ring current and shifted upfield by ~-0.7 ppm. However, the protons **(f)** and **(i)** are slightly deshielded relative to the analogous protons on [G-3]-OH.

It is clear that all protons more remote from the central silicon atom than protons **(f)** are deshielded relative to [G-3]-OH. An analysis of the molecular structure of **(45)** obtained by X-ray crystallography (Fig. 3.4) may help to explain this initially surprising result.

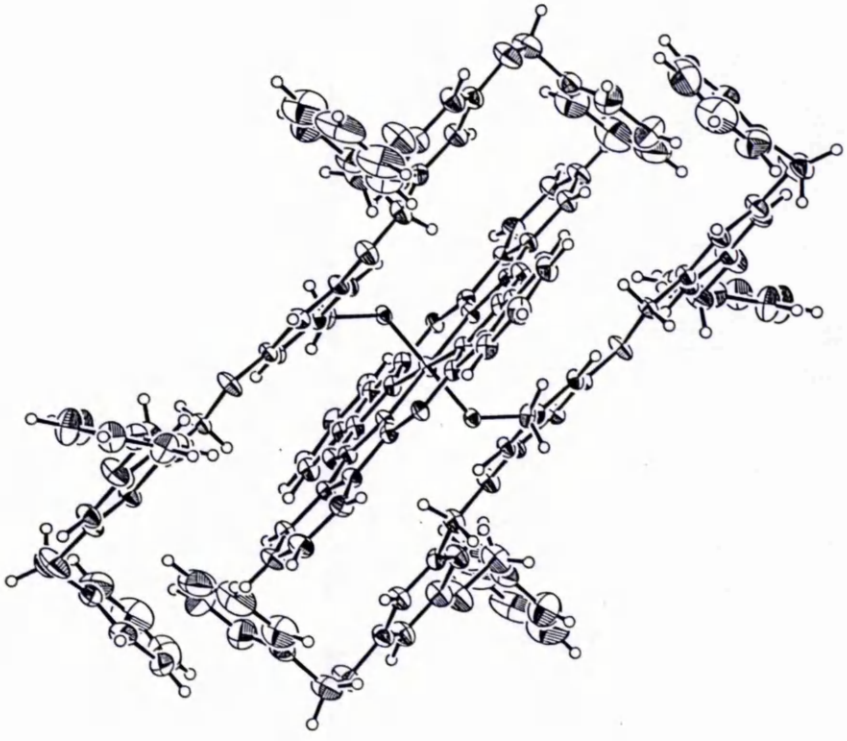


Fig. 3.4 Totally Flattened View of Pc **(45)**

It can be seen that the outer layers of the dendritic wedge are draped over the edge of the Pc macrocycle. This would result in a deshielding effect for these portions. In solution the wedges are likely to be relatively mobile, and the resulting position of the protons an average of all the possible positions relative to the ring current. Nevertheless, the more remote protons are likely to spend more time in the deshielding region of the induced magnetic field.

The exterior phenyl protons **(k)** occur between 7.20 and 7.40 ppm in all three axial Pcs, similar to their position in [G-3]-OH which suggests that the ring current is having no significant effect at this distance. The peripheral and non-peripheral protons on the Pc ring **(l)** and **(m)** show the

same chemical shift in all three of the Pcs and all show the classic AA'XX' multiplet splitting pattern.

3.1.2 UV/ visible Absorption Spectra

The characteristic solution UV/vis absorption spectrum for a typical metal-free Pc is given in Fig. 1.1. A strong absorption is seen between 670 and 690 nm termed the Q-band, and between 320 and 370 nm, denoted as the B or Soret band. The former absorption is responsible for the characteristic intense blue (or blue-green) colour of the compound. The Q-band is also partially sensitive to substitution and the environment which the Pc macrocycle is in. A typical value of the extinction coefficient of the Q-band is 2×10^5 cm^2 $mole^{-1}$ and the weak absorption bands at $\approx$ 600 nm are the vibrational overtones of the Q-band. The electronic molecular orbital structure of a typical MPc has been mapped by Gouterman[4] and the important Q-band absorption has been assigned to a $\pi - \pi^*$ transition from the highest occupied molecular orbital (HOMO), of a a_{1u} symmetry, to the lowest unoccupied orbital (LUMO) of e_g symmetry. This results in a doubly degenerate first excited state of ^1E_u symmetry. The split Q-band obtained from H_2Pc is due to the lower symmetry (D_{2h}), as compared to that of planar MPcs (D_{4h}), and the consequent loss of degeneracy of the LUMO orbital to produce the Q_y and Q_x states. The more complicated orbital energy arrangement of H_2Pc has been described in detail by Orti[5] and recently reviewed.[6] The splitting of the Q-band is lost on deprotonation, using a strong base (e.g. tetrabutyl ammonium hydroxide), to form the Pc^{2-} anion which also has D_{4h} symmetry.

Non-peripheral substitution, in particular, can influence greatly the energy levels of the molecular orbital and hence the absorption spectrum. Electron donating groups such as alkoxy moieties cause a *bathochromic shift* (red-shift) of the Q-band, by raising the energy level of the HOMO, a_{1u} level.[7] In contrast, most peripheral substitution has very little effect on Q-band position. An exception is when the substituents result in an extension of the π-orbital system such as in naphthalocyanine or anthracene. These show bathochromic shifts of 90 nm and 170 nm respectively.[8]

The extent of Pc aggregation in the bulk and solution phase can be assessed by UV/vis absorption spectroscopy. Excitonic interactions cause a shift of the monomer Q-band (~680 nm) to shorter wavelengths, whereas edge-to-edge interactions shift the Q-band to longer wavelengths. A non-axially substituted Pc will give a Q-band at ~620 nm due to cofacial interactions, but dendritic axial substitution gives Pcs which are red-shifted due to edge-to-edge effects (Table 3.3).

Substituted Pc	**44**	**45**	**46**
λ_{max} soln (nm)	678	680	680
λ_{max} solid (nm)	704	692	688

Table 3.3 UV/vis absorption data of axially substituted Pcs **(44)**, **(45)** and **(46)**

Table 3.3 gives the bulk spectroscopic data for each of the axially substituted dendrimers. It shows clearly that as the size of the dendritic substituent increases, the Pc spectra come to resemble the non-aggregated solution spectrum due to the reduction in edge-to-edge interactions of the

Pc cores. In contrast the peripherally substituted Pcs **(9)-(11)** all gave spin coated films with λ_{max} = 630 nm consistent with strong cofacial interactions.

3.2 Single Crystal X-Ray Diffraction (XRD)

The ability of H_2Pc and its planar metal derivatives to form crystals by vacuum sublimation led to their structure determination by X-ray diffraction.[9] In addition, these studies showed that the common crystal type obtained by sublimation, subsequently termed the β-form, was monoclinic belonging to the $P2_1/a$ space group with two Pc molecules per unit cell. Single crystal XRD studies are still of great importance for the understanding of the properties of Pc materials.

Suitable crystals of the [G-2] axially substituted phthalocyanine **(45)** were prepared by the slow diffusion of diethyl ether into a concentrated toluene solution. An X-ray diffraction study revealed the beautiful molecular crystallographic structure of this molecule. The crystal is triclinic and of the P1 (#2) space group. The asymmetric unit consists of half a molecule with the Si atom lying on a centre of symmetry and the other half generated by inversion (Fig. 3.5 and appendix 1).

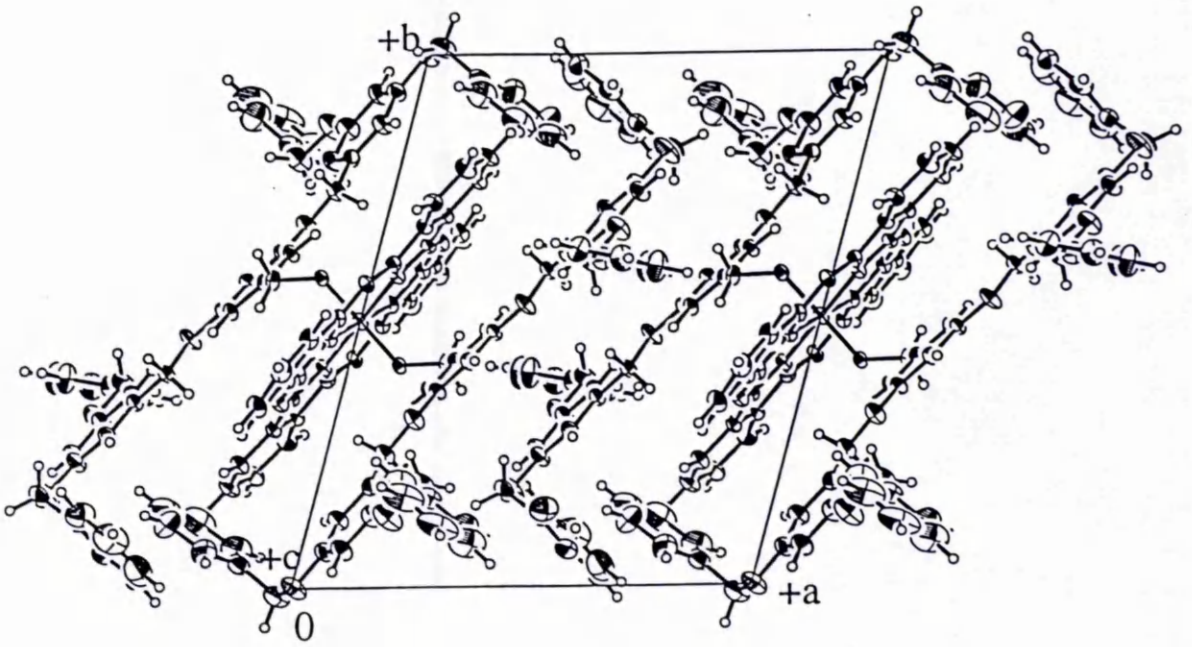


Fig. 3.5 Stacking of Pc **(45)**

3.3 Thermal Behaviour of the Novel Phthalocyanine Materials

3.3.1 Thermal Behaviour of Axially Substituted Phthalocyanines : The Formation of Isotropic Pc Glasses

In polymers, when the temperature is sufficiently low that the large scale motion of the polymer chains is no longer possible (and crystallisation has not occurred), glasses are formed from the liquid-like state. This results in small groups or singular atoms moving against local restraints of

secondary bond forces.

Isotropic glassy solids based on low molar mass Pcs have been produced by placing bulky groups directly onto the macrocycle.[10] For this system, cofacial association is apparent from the UV/vis absorption spectrum. Each of the axially substituted Pcs **(44)-(46)** displays a distinct glass transition on cooling from the melt (T_g = 139, 124 and 104°C respectively, Fig 3.6).

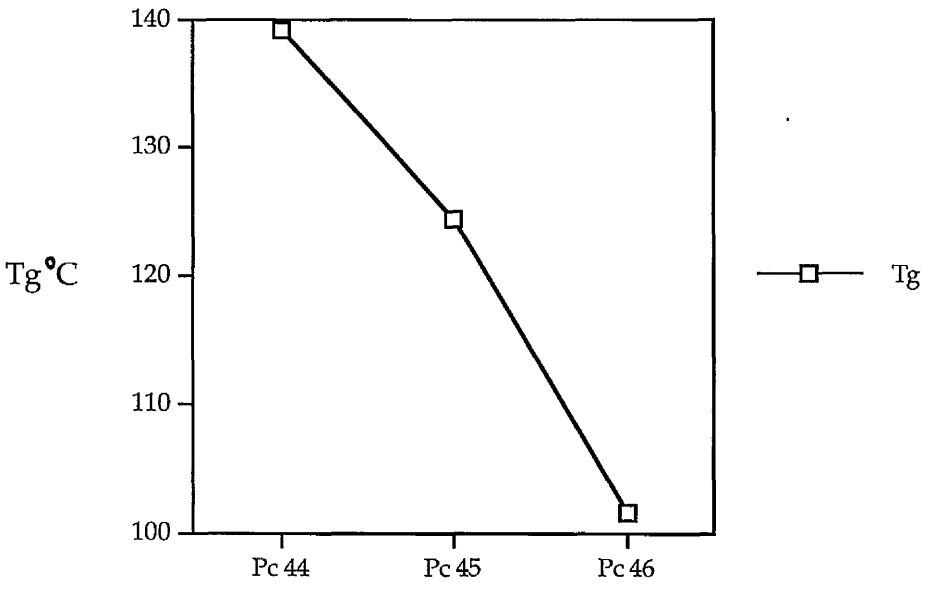


Fig. 3.6 Graph of transition temperature vs degree of substitution for axially substituted phthalocyanines **(44)**, **(45)** and **(46)**

These glasses differ from those formed from peripherally substituted Pcs in that cofacial association will be prevented by the axial substituents (see Table 3.3). Therefore, amorphous films can be fabricated from Pcs **(44)-(46)** by melt processing in addition to spin coating. These glassy

materials are robust, non-scattering, and appear indefinitely stable towards crystallisation. They may be useful materials for optical studies.

3.3.2 Thermal Behaviour of Pcs Peripherally Substituted with Dendritic Wedges : The Formation of Columnar Glasses

The unsymmetrical dendritically substituted phthalocyanines **(33)-(37)** possess at least a single discotic hexagonal (D_h) mesophase over a broad temperature range (Table 3.4 and Fig. 3.2, see also appendix 2 and 3).

Pc	K → D_h	Glass → D_h	D_h → I
(9)	115 °C[a]		270 °C
(10)	106 °C[a]		248 °C
(28)	98 °C[a]		234 °C
(35)		115.7 °C[b]	250 °C - 255 °C
(37)		103.4 °C[b]	108 °C - 112 °C
(36)		93.5 °C[b]	134 °C - 137 °C

Table 3.4 Transition temperatures °C

N.B. Transition temperatures quoted are for the heating cycle.
(a) transition temperatures measured only by optical microscopy,
(b) onset of glass transition observed by DSC on heating the sample.

Each compound on cooling from its isotropic phase, forms a fluid mesophase. This is mainly homeotropic when viewed using a polarising microscope, but displays birefringent fan like defects. This texture is characteristic of a columnar mesophase which has a two dimensional

lattice of hexagonal symmetry, but in which there is no periodicity of molecular spacing along the columnar axes (D_{hd}). The D_{hd} mesophase is commonly encountered for phthalocyanine mesogens (see appendix 3), especially those substituted by alkyl side chains such as the symmetrical by-products of the mixed phthalonitrile reactions (Fig. 3.7).

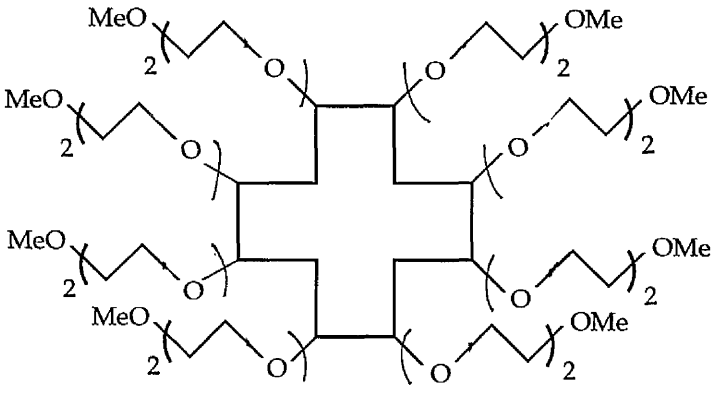


Fig 3.7 Symmetrical by-product of the mixed phthalonitrile reactions.

Noting the relatively inflexible and bulky nature of the dendrimer substituent, it is remarkable that the mixed dendritic phthalocyanines possess liquid crystallinity over such broad temperature ranges. In addition to reducing the clearing temperature, the dendritic substituents appear to induce the formation of a glassy solid as the Pcs displays only glass transitions (Tg) rather than true melting points. This is clear from the DSC analysis of Pc **(37)** (Fig. 3.8). The values of the glass transition temperatures (Tg) are given in Table 3.4. Values for Tg of the [G-1] substituted mixed phthalocyanines **(33)** and **(34)** were not obtained, possibly due to the glassy solids forming too slowly to enable a Tg to be seen by DSC.

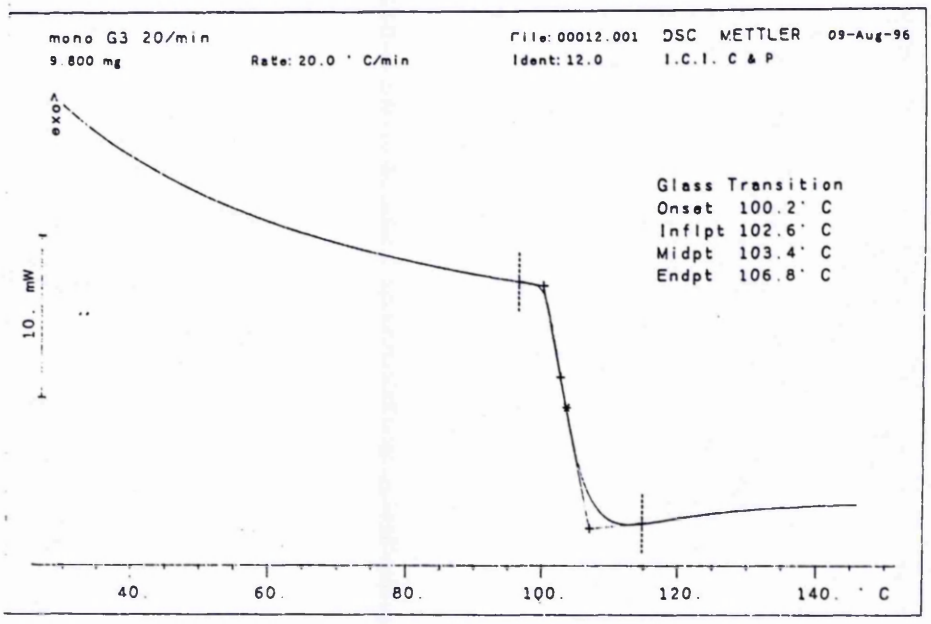


Fig. 3.8 DSC of Pc **(37)** clearly showing Tg.

It has been shown previously that glass formation in discotic mesophases is associated with the loss of motion about the columnar axis.[11] For Pc mesogens this can be encouraged by the use of bulky substituents such as trityl groups.[12] The distinct glassy state exhibited by the peripherally substituted Pcs **(35)-(37)** is a useful material property as it can be used to freeze the structure of the columnar mesophase into the solid state. These columnar glasses display by far the highest glass transition temperature of any non-polymeric discotic systems and could be useful for the study of anisotropic conductivity.

3.3.3 X-Ray Diffraction (XRD) Studies on Columnar Mesophases and Anisotropic Glasses

X-ray diffraction is an excellent technique for determining the structure of columnar mesophases, giving diffraction patterns based on the repeat distances of the columnar lattice arrangement.[13] Much more structural information can be obtained from liquid crystalline samples that are uniformly oriented. However, the highly viscous mesophases displayed by Pc derivatives make alignment into a single domain difficult and most XRD studies have been carried out on non-oriented (powder) samples. Mesophases which are structurally assigned only from microscopic textures are questionable.

Only one strong diffraction ring is observed from the X-ray powder study of the series of unsymmetrical Pcs **(33)-(37)** in either their mesomorphic or glassy solid states (see appendix 2). Therefore, there is no direct evidence (i.e. no second 110 diffraction ring), of a hexagonal structure from the X-ray data to confirm the conclusions derived from optical microscopy. The lack of (110) diffraction however, indicates disorder as would be expected from these unsymmetrical molecules. In addition, there was no evidence of wide-angle diffractions which indicates disorder along the axis of the molecular columns. The single diffraction ring can be used to measure the intercolumnar distances (Table 3.5 and Fig. 3.9) for the liquid crystals, (see also appendix 2).

For each material, the general appearance of the diffraction pattern obtained at room temperature in the solid phase is almost identical to that obtained in the mesophase. This is further evidence that columnar glasses

are formed on cooling, as crystallisation would result in the observation of many more diffraction rings

Pc	Temp °C	d_1 Å	d_i Å
Mono [G-1] **(33)**	25	23.8	27.48
Mono [G-1] **(33)**	150	24.3	28.06
Di [G-1] **(34)**	25	24.4	28.18
Di [G-1] **(34)**	150	25	28.87
Mono [G-2] **(35)**	25	25.5	29.45
Mono [G-2] **(35)**	150	26	30.02
Di [G-2] **(36)**	150	29.1	33.60
Mono [G-3] **(37)**	25	29.9	34.53

Table 3.5 Table of intercolumnar distances (d_i) obtained from X-ray diffraction data.

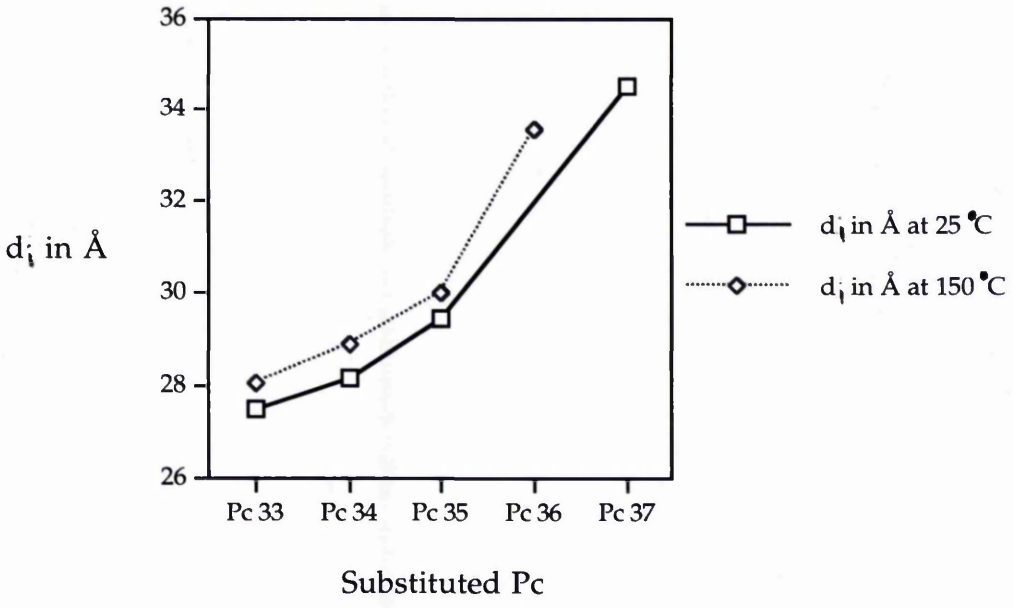


Fig. 3.9 Graph of intercolumnar distance vs degree of substitution at varying temperatures for Pcs **(33)-(37)**

3.4 Chapter Three References

1. Kane, A. R., Sullivan, J. F., Kenny, D. H., Kenney, M. E., *Inorg. Chem.*, 1970, 9, 1445

2. Janson, T. R., Kane, A. R., Sullivan, J. F., Knox, K., Kenney, M. E., *J. Am. Chem. Soc.*, 1969, 91, 5210

3. Kane, A. R., Yalman, R. G., Kenney, M. E., *Inorg. Chem.*, 1968, 7, 2588

4. Dolphin, D., *'The Porphyrins. Volumes I-VIII,'* New York, Academic Press, 1978

5. Ortí, E., Brédas, J. L., Clarisse, C., *Journal of Chemical Physics*, 1990, 92, 1228-35

6. Cook, M. J., in *'Spectroscopy of New Materials,'* Ed. R. J. H. Clark & R. H. Hester, London, John Wiley and Sons, 1993, pp. 87-150

7. Cook, M. J., Dunn, A. J., Howe, S. D., Thomson, A. J., Harrison, K. J., *Journal of the Chemical Society, Perkin Trans.1*, 1988, 2453-8

8. Kobayashi, N., Nakajima, S., Osa, T., *Inorganica Chimica Acta*, 1993, 210, 131-3

9. Robertson, J. M., *Journal of the Chemical Society*, 1935, 615-21

10. George, R. D., Snow, A. W., *Chemistry of Materials*, 1994, 6, 1587-8

11. Möller, M., Wendorff, J. H., Werth, M., Speiss, H. W., *J. Non-Cryst. Solids*, 1994, 170, 295

12. Treacher, K. E., Clarkson, G. J., McKeown, N. B., *Liquid Crystals*, 1995, 19, 887

13. Cherodian, A. S., Davies, A. N., Richardson, R. M., Cook, M. J., McKeown, N. B., Thomson, A. J., Feinjoo, J., Ungar, G., Harrison, K. J., *Molecular Crystals and Liquid Crystals*, 1991, 196, 103-14

4

Experimental

4.1 Experimental

4.1.1 Equipment and Materials

Routine ^1H NMR spectra were measured at 200 MHz using a Varian Gemini 200 spectrometer. High resolution (500 MHz) ^1H NMR spectra were recorded using a Varian Unity 500 spectrometer. UV-visible spectra were recorded on a Shimadzu UV-260 spectrophotometer from either a solid film or toluene solutions using cells of pathlength 10 mm. IR spectra were recorded from KBr discs on a ATI Mattson Genesis Series FTIR (KBr/Germanium beam splitter). Elemental analyses were obtained using a Carlo Erba Instrument CHNS-O EA 108 Elemental Analyser. Routine low resolution chemical ionisation (CI) and electron ionisation (EI) were obtained using a Fisons instrument Trio 2000. Phthalocyanine fast atom bombardment (FAB) spectra were recorded on a Kratos Concept spectrometer. Routine melting point determination was carried out with a Gallenkemp melting point apparatus and melting points are uncorrected. Determination of transition temperatures, crystal (K) to mesophase (D_{ho}) to isotropic liquid (I) were obtained by optical microscopy using a Nikon Optiphot-2 microscope in conjunction with a Mettler FP82HT hot stage and were confirmed by differential scanning calorimetry (DSC) using a Mettler DSC 20 oven and TC 11 processor. All solvents were dried and purified as described in Perrin and Armarego.[1] Silica gel (60 Merck 9385) was used in the separation and purification of dendrimers, phthalonitriles and phthalocyanines by column chromatography.

4.2 Synthesis of Dendritic Wedges

4.2.1 Synthesis of 3,5-dibenzyloxybenzyl alcohol, *[G-1]-OH*

(a) Synthesis of methyl-3,5-dihydroxybenzoate[2]

Sulphuric acid (1 ml) was added to 3,5-dihydroxybenzoic acid (50 g, 324 mmol) in MeOH (250 ml). The solution was heated at reflux overnight, cooled and concentrated under reduced pressure to a quarter of its original volume. The reaction mixture was neutralised with aqueous sodium bicarbonate (600 ml) and the aqueous layer extracted with EtOAc (3x 100 ml). The organic layers were combined and evaporated to dryness under reduced pressure to afford pure *methyl-3,5-dihydroxybenzoate* as a white powder; (52 g, 95 % yield); m.p. 97-98 °C; δ_H (200 MHz, $CDCl_3$) 3.90 (3H, s), 6.68 (2H, d), 6.78 (1H, t), 7.15 (2H, s).

(b) Synthesis of methyl-3,5-dibenzyloxybenzoate[3]

A mixture of methyl-3,5-dihydroxybenzoate (66 g, 393 mmoles), benzyl chloride (105 g, 806 mmoles) potassium carbonate (115 g, 832 mmoles) and acetone (250 ml) was stirred at reflux for 48 hours. The mixture was cooled filtered to remove inorganic salts and concentrated *in vacuo*. The residue was redissolved in EtOAc and washed with aqueous sodium hydroxide (3x 100 ml). The organic layer was separated and dried over magnesium sulphate, filtered and concentrated under reduced pressure to yield a crude yellow oil, which recrystallised from petroleum ether to afford pure *methyl-3,5-dibenzyloxybenzoate* as white needles; (128 g, 94 % yield); m.p. 85-86 °C; δ_H (200 MHz, $CDCl_3$) 3.90 (3H, s), 4.97 (4H, s),

6.52 (1H, t), 6.59 (2H, d), 7.30-7.40 (10H, m).

(c) Synthesis of 3,5-dibenzyloxybenzyl alcohol, [G-1]-OH[3, 4]

A solution of methyl-3,5-dibenzyloxybenzoate (8 g, 23 mmoles) in dry THF (200 ml), was added over 20 minutes via a dropping funnel to a stirred solution of $LiAlH_4$ (1.3 g, 34 mmoles) in dry THF (300 ml) at a rate to maintain a constant reflux. The reaction mixture was stirred at room temperature overnight, until TLC analysis (toluene : 10 % EtOAc) indicated no starting methyl ester. Water (1 ml) was slowly added, followed by 15 % NaOH solution (1 ml) and a further portion of water (3 ml) to completely destroy any remaining $LiAlH_4$. The solution was stirred for a further hour. It was then filtered and evaporated to dryness under reduced pressure. The crude product was recrystallised twice from DCM : petroleum ether (3 : 1) to afford pure *3,5-dibenzyloxybenzyl alcohol, ([G1]-OH)* as white needles; (6.8 g, 92 % yield); m.p. 110-111 °C; δ_H (500 MHz, $CDCl_3$) 4.64 (3H, d), 5.05 (4H, s), 6.56 (1H, t), 6.65 (2H, d), 7.30-7.48 (10H, m).

4.2.2 Synthesis of *3,5-dibenzyloxybenzyl bromide, [G-1]-Br*[3]

Triphenylphosphine (2.56 g, 9.8 mmoles) in DCM (5 ml) was added over 30 minutes to a solution of [G-1]-OH (2.5 g, 7.8 mmoles) and carbon tetrabromide (3.23 g, 9.7 mmoles) in DCM (5 ml) under an atmosphere of nitrogen. The reaction mixture was stirred at room temperature for one hour, after which time the mixture was poured into water and the product extracted with DCM (3x 50 ml). The organic extracts were combined, dried over magnesium sulphate and evaporated to dryness under reduced

pressure to afford a yellow oil. Purification was achieved by column chromatography (silica, toluene : 10 % EtOAc) and the band at $R_f = 0.65$ collected. The product was recrystallised from toluene : hexane (3 : 1), to afford pure *3,5-dibenzyloxybenzyl bromide ([G-1]-Br)* as a white powdery solid; (2.9 g, 97 % yield); m.p. 92-93 °C; δ_H (500 MHz, $CDCl_3$) 4.41 (2H, s), 4.97 (4H, s), 6.54 (1H, t), 6.60 (2H, d), 7.28-7.45 (10H, m).

4.2.3 Synthesis of *[G-2]-OH* [4]

Anhydrous potassium carbonate (0.72 g, 5.20 mmoles), 3,5-dihydroxybenzyl alcohol (0.29 g, 2.07 mmoles), [G-1]-Br (2.0 g, 5.22 mmoles), and 18-crown-6 (0.11 g, 0.42 mmoles) in freshly distilled dry acetone (50 ml) were vigorously stirred at reflux under a nitrogen atmosphere for 72 hours. The mixture was allowed to cool and then evaporated to dryness under reduced pressure. The residue was redissolved in water (100 ml) and extracted with DCM (3x 50 ml). The combined organic extracts were dried, evaporated to dryness to leave a brown oil which was purified by flash column chromatography (silica, toluene : 10 % EtOAc). The product was recrystallised from toluene : hexane (3 : 1), to afford pure *[G-2]-OH* as a white crystalline solid; (2.55 g, 85.1 % yield); m.p. 110-111 °C; δ_H (500 MHz, $CDCl_3$) 4.62 (3H, d), 4.97 (4H, s), 5.02 (8H, s), 6.52 (1H, t), 6.57 (2H, t), 6.59 (2H, d), 6.67 (4H, d), 7.29-7.42 (20H, m).

4.2.4 Synthesis of *[G-2]-Br* [4]

The procedure was the same as that described for the synthesis of [G-1]-Br. Triphenylphosphine (0.44 g, 1.68 mmoles) in DCM (3 ml) was

added to carbon tetrabromide (0.56 g, 1.68 mmoles) and [G-2]-OH (1 g, 1.3 mmoles) in DCM (10 ml). Purification was achieved by flash column chromatography (silica, toluene) and the band at $R_f = 0.7$ collected. The product was recrystallised from toluene : hexane (3 : 1) to afford pure *[G-2]-Br* as a white solid; (0.15 g, 13.8 % yield); m.p. 120-130 °C; δ_H (500 MHz, $CDCl_3$) 4.41 (2H, s), 4.97 (4H, s), 5.04 (8H, s), 6.53 (1H, t), 6.59 (2H, t), 6.63 (2H, d), 6.68 (4H, d), 7.30-7.44 (20H, m).

4.2.5 Synthesis of *[G-3]-OH* [4]

The procedure was the same as that described for the synthesis of [G-2]-OH using 3,5-dihydroxybenzyl alcohol (0.007 g, 0.05 mmoles), [G-2]-Br (0.1 g, 0.12 mmoles), anhydrous potassium carbonate (0.016 g, 0.12 mmoles) and 18-crown-6 (0.003 g, 0.01 mmoles). Purification was achieved by flash column chromatography (silica, toluene : 10 % EtOAc) and the band at $R_f = 0.75$ collected. Evaporation to dryness was performed under reduced pressure to afford pure *[G-3]-OH* as a colourless glass; (0.05g, 25 % yield); δ_H (500 MHz, $CDCl_3$) 4.57 (3H, d), 4.94 (12H, s), 5.00 (16H, s), 6.36 (3H, m), 6.39 (4H, t), 6.42 (2H, d), 6.48 (4H, d), 6.50 (8H, d), 7.27-7.41 (40H, m).

4.3 Synthesis of Dendritic Wedges via the Ester Route[5]

4.3.1 Synthesis of *[G-2] methyl ester*

A mixture of [G-1]-OH (5.0 g, 15.6 mmoles), methyl-3,5-dihydroxybenzoate (1.19 g, 7.1 mmoles) and DCCI[6] (3.22 g, 15.6 mmoles) was heated at 80 °C under an atmosphere of nitrogen for 72 hours until TLC analysis (toluene : 10 % EtOAc) indicated no starting ester remained. Purification was achieved by column chromatography (silica, toluene) and the band at $R_f = 0.6$ collected. Evaporation to dryness under reduced pressure afforded pure *[G-2] methyl ester* as a white solid; (4.2 g, 76.8 % yield); m.p. 129-130°C; IR (KBr disc) 1730.0, 1650.5, 1597.8, 1438.3, 1365.0, 1164.0, 1070.0 cm^{-1}; Found C, 77.90 %; H, 5.63 %; $C_{50}H_{44}O_8$ requires C, 77.70 %; H, 5.73 %; δ_H (200 MHz, $CDCl_3$) 3.90 (3H, s), 4.98 (4H, s), 5.02 (8H, s), 6.55 (2H, t), 6.68 (6H, d), 6.78 (1H, t), 7.29-7.45 (20H, m); MS (EI/CI) found *m/e* 773, (M^+) requires 773.

4.3.2 Synthesis of *[G-2]-OH via $LiAlH_4$ reduction of [G-2]-methyl ester*

The procedure was the same as that described for the synthesis of 3,5-dibenzyloxybenzyl alcohol ([G-1]-OH) using $LiAlH_4$ (0.12 g, 3.2 mmoles) in dry THF (100 ml) and [G-2] methyl ester (2.45 g, 3.17 mmoles) in dry THF (100 ml). Crystallisation and recrystallisation from toluene : hexane (3 : 1) afforded pure *[G-2]-OH* as white needles; (2.0 g, 84.7 % yield); m.p. 110-111 °C.[4]

4.4 Synthesis of Dendritic Wedges Containing Alkyl Spacers

4.4.1 Synthesis of *[G-1]-OH with ethylene spacer*

Sodium hydride (0.23 g, 60 % dispersion in oil, 5.9 mmoles) was added to an ice cooled solution of ethylene glycol (10 ml, 10.2 g, 164 mmoles) in dry THF (40 ml) under an atmosphere of nitrogen. After the exotherm had resided, [G-1]-Br (0.75 g, 1.95 mmoles) was added. The reaction mixture was warmed to 50 °C and stirred for 12 hours. Water (10 ml) was then carefully added and the THF removed under reduced pressure. The reaction mixture was partitioned between 1M hydrochloric acid (50 ml) and toluene (30 ml) and the aqueous layer further extracted with toluene (2x 30 ml). The combined organic extracts were washed with water (50 ml), dried over magnesium sulphate and filtered. Purification was achieved by column chromatography (silica, petroleum ether : 75 % diethyl ether) and the band at $R_f = 0.4$ collected. Evaporation to dryness was performed under reduced pressure to afford pure *2-(3',5'-dibenzyloxy)benzyloxyethanol* as a colourless oil; (0.59 g, 83 % yield); Found C, 75.71 %; H, 7.05 %; $C_{23}H_{24}O_4$ requires C, 75.80 %; H, 6.64 %; δ_H (200 MHz, $CDCl_3$) 2.00 (1H, t), 3.57 (2H, t), 3.75 (2H, m), 4.51 (2H, s), 5.05 (4H, s), 6.57 (1H, t), 6.63 (2H, d), 7.48-7.55 (10H, brm); MS (CI) found *m/e* 382, $(MNH_4)^+$ requires 382.

4.4.2 Synthesis of *[G-2]-OH with ethylene spacer*

The procedure was the same as that described for the synthesis of 2-(3',5'-dibenzyloxy)benzyloxyethanol using sodium hydride (0.19 g, 60 %

dispersion in oil, 4.68 mmoles), an ice cooled solution of ethylene glycol (5 ml, 5.1 g, 8.2 mmoles) in dry THF (40ml) and [G-2]-Br (1.26 g, 1.56 mmoles). Purification was achieved by column chromatography (silica, toluene : 10 % EtOAc) and the band at $R_f = 0.6$ collected. Crystallisation and recrystallisation from toluene : hexane (3 : 1) afforded pure *2'-(3',5'-di(3'',5''-dibenzyloxy)benzyloxy)benzyloxy ethanol* as white needles; (0.80 g, 65 % yield); m.p. 95-96 ° C; Found C, 77.75 %; H, 6.45 %; $C_{51}H_{48}O_8$ requires C, 77.64 %; H, 6.13 %; δ_H (200 MHz, $CDCl_3$) 2.02 (1H, t), 3.58 (2H, t), 3.75 (2H, m), 4.50 (2H, s), 4.99 (4H, s), 5.05 (8H, s), 6.55 (1H, t), 6.59 (4H, m), 6.69 (4H, d), 7.48-7.55 (20H, brm); MS (CI) found *m/e* 807, $(MNH_4)^+$ requires 807.

4.4.3 Synthesis of *methyl-4,4-bis(4'-(benzyloxy)phenyl) pentanoate*[7]

A mixture of methyl-4,4-bis(4'-hydroxyphenyl) pentanoate (30.0 g, 105 mmoles), benzyl chloride (24.1 g, 190 mmoles), potassium carbonate (28.9 g, 209 mmoles), DMF (200 ml) and a catalytic amount of sodium iodide were stirred at reflux for 48 hours. The reaction mixture was cooled, filtered to remove the inorganic salts and concentrated under reduced pressure. The residue was redissolved in EtOAc, poured into water and the aqueous layer extracted with EtOAc (3x 100 ml). The organic layer was dried over magnesium sulphate, filtered and evaporated to dryness under reduced pressure to afford *methyl-4,4-bis(4'-(benzyloxy)phenyl)pentanoate* as a dark yellow oil; (41.1 g, 81.2 % yield); δ_H (200 MHz, $CDCl_3$) 1.62 (3H, s), 2.19 (2H, m), 2.45 (2H, m), 3.68 (3H, s), 4.98 (4H, s), 6.90 (4H, d), 7.15 (4H, d), 7.35-7.50 (10H, brm).

4.4.4 Synthesis of *4,4-bis(4'-(benzyloxy)phenyl) pent-1-ol*

The procedure was the same as that described for the synthesis of dibenzyl 3,5-dihydroxybenzoate using $LiAlH_4$ (0.81 g, 21.3 mmoles) in dry THF (100 ml) and methyl-4,4-bis(4'-(benzyloxy)phenyl) pentanoate (10 g, 21.3 mmoles) in dry THF (50 ml). Purification was achieved by column chromatography (silica, toluene) and the band at $R_f = 0.75$ collected. Evaporation to dryness was performed under reduced pressure to afford pure *4,4-bis(4'-(benzyloxy)phenyl) pent-1-ol* as a colourless oil; (7.8 g, 81 % yield); IR (evaporated film) 3032.0, 2924.3, 2868.7, 1598.3, 1496.2, 1374.3, 1241.8, 1154.9, 1028.4 cm^{-1}; Found C, 82.04 %; H, 7.20 %; $C_{31}H_{32}O_3$ requires C, 82.27 %; H, 7.13 %; δ_H (200 MHz, $CDCl_3$) 1.50 (1H, t), 1.65 (3H, s), 2.19 (2H, m), 2.45 (2H, m) 2.60 (2H, m), 4.98 (4H, s), 6.90 (4H, d), 7.15 (4H, d), 7.35-7.45 (10H, m); MS (EI/CI) found *m/e* 453, (M^+) requires 453.

4.4.5 Synthesis of *methyl-4,4-bis(4'-(3'',5''-dibenzyloxy) benzyloxyphenyl) pentanoate*

Methyl-4,4-bis(4'-hydroxyphenyl) pentanoate (9.2 g, 6.66 mmoles), [G-1]-OH (4.69 g, 15 mmoles) and DCCI[6] (3.0 g, 15 mmoles) were heated with stirring at 80 °C under an atmosphere of nitrogen for 96 hours until TLC analysis (toluene) indicated no starting dendrimer remained. Purification was achieved by column chromatography (silica, toluene) and the band at $R_f = 0.45$ collected. Evaporation to dryness was performed under reduced pressure to afford pure *methyl-4,4-bis(4'-(3'',5''-dibenzyloxy)benzyloxyphenyl) pentanoate* as a yellow oil; (3.98 g, 66 % yield); IR (evaporated film) 3033.0, 2929.5, 2866.2, 1597.6, 1507.6, 1451.1, 1375.4, 1244.0, 1156.8, 1025.3 cm^{-1}; Found C, 79.18 %; H, 6.19 %; $C_{60}H_{56}O_8$

requires C, 79.63 %; H, 6.24 %; δ_H (200 MHz, $CDCl_3$) 1.62 (3H, s), 2.19 (2H, m), 2.45 (2H, m), 3.68 (3H, s), 4.98 (4H, s), 5.18 (8H, s), 6.62 (2H, t), 6.74 (4H, t), 6.90 (4H, d), 7.15 (4H, d), 7.35-7.50 (20H, brm); MS (FAB) found *m/e* 905, (M^+) requires 905.

4.4.6 Synthesis of *4,4-bis(4'-(3'',5''-dibenzyloxy)benzyloxyphenyl) pent-1-ol*

The procedure was the same as that described for the synthesis of dibenzyl 3,5-dihydroxybenzoate using $LiAlH_4$ (0.163 g, 4.3 mmoles) in dry THF (100 ml) and methyl-4,4-bis(4'-(3",5"-dibenzyloxy) benzyloxyphenyl)pentanoate (3.90 g, 4.3 mmoles) in dry THF (50 ml). Purification was achieved by column chromatography (silica, 20 % EtOAc : toluene) and the band at R_f = 0.55 collected. Evaporation to dryness was performed under reduced pressure to afford pure *4-bis(4'-(3'',5''-dibenzyloxy)benzyloxyphenyl) pent-1-ol* as a yellow oil; (3.64 g, 94 % yield); IR (evaporated film) 3033.0, 2926.5, 2869.5, 1599.3, 1507.3, 1452.9, 1376.1, 1243.4, 1157.7, 1027.4 cm^{-1}; Found C, 80.65 %; H, 6.20 %; $C_{59}H_{56}O_7$ requires C, 80.80 %; H, 6.44 %; δ_H (200 MHz, $CDCl_3$) 1.35-1.48 (2H, m), 1.50 (1H, t), 1.65 (3H, s), 3.60 (2H, m), 4.98 (4H, s), 5.18 (8H, s), 6.60 (2H, t), 6.72 (4H, t), 6.90 (4H, d), 7.15 (4H, d), 7.28-7.50 (20H, brm); MS (FAB) found *m/e* 877, (M^+) requires 877.

4.5 Synthesis of Phthalonitrile Precursors Based on 4-Nitrophthalonitrile

4.5.1 Synthesis of *[G-1]-Phthalonitrile, [G-1]-Pn* (1)

[G-1]-OH (2.0 g, 6.25 mmoles), 4-nitrophthalonitrile (1.41 g, 8.15 mmoles), potassium carbonate (1.12 g, 8.1 mmoles) and DMF (5 ml) were stirred at 60 °C for 48 hours. The reaction mixture was cooled and poured into water (100 ml). The aqueous layer was extracted with DCM (3x 50 ml), dried over magnesium sulphate and filtered. The organic layer was evaporated to dryness, leaving a green oil. Purification was achieved by column chromatography (silica, toluene : 10 % EtOAc) and the band at $R_f = 0.7$ collected. Evaporation to dryness was performed under reduced pressure to afford pure *[G-1]-Pn* as a yellow powdery solid; (2.5 g, 90 % yield); m.p. 114-116 °C; IR (KBr disc) 2923.0, 2853.5, 2227.5, 1597.8, 1498.3, 1164.0 cm^{-1}; Found C, 77.9 %; H, 5.03 %; N, 6.4 %; $C_{29}H_{22}O_3N_2$ requires C, 78.01 %; H, 4.97 %; N, 6.27 %; δ_H (500 MHz, $CDCl_3$) 5.05 (4H, s), 5.10 (2H, s), 6.58 (1H, t), 6.60 (2H, d), 7.15 (1H, dd), 7.25 (1H, d), 7.29-7.45 (10H, m), 7.65 (1H, d); MS (EI/CI) found *m/e* 446, (M^+) requires 446.

4.5.2 Synthesis of *[G-2]-Phthalonitrile, [G-2]-Pn* (2)

The procedure was the same as that described for the synthesis of [G-1]-Pn using [G-2]-OH (0.2 g, 0.27 mmoles), 4-nitrophthalonitrile (0.06 g, 0.35 mmoles), potassium carbonate (0.048 g, 0.035 mmoles) and DMF (1 ml). Purification was achieved by column chromatography, (silica, toluene : 10 % EtOAc) and the band at $R_f = 0.75$ collected. Evaporation of the solvent under reduced pressure afforded *[G-2]-Pn* as a colourless oil

(0.46 g, 85 % yield); IR (KBr disc) 2928.4, 2231.2, 1596.5, 1497.3, 1158.0 cm^{-1}; Found C, 76.93 %; H, 6.39 %; N, 2.59 %; $C_{57}H_{46}O_7N_2$ requires C, 78.60 %; H, 5.32 %; N, 3.22 %; δ_H (500 MHz, $CDCl_3$) 4.97 (4H, s), 5.02 (8H, s), 5.08 (2H, s), 6.52 (1H, t), 6.57 (2H, t), 6.59 (2H, d), 6.67 (4H, d), 7.14 (1H, dd), 7.23 (1H, d), 7.29-7.42 (20H, m), 7.595 (1H, d); MS (EI/CI) *m/e* 871, (M^+) requires 871.

4.5.3 Synthesis of *[G-3]-Phthalonitrile, [G-3]-Pn* (3)

The procedure was the same as that described for the synthesis of [G-1]-Pn using [G-3]-OH (0.1 g, 0.06 mmoles), 4-nitrophthalonitrile (0.014 g, 0.08 mmoles), potassium carbonate (0.011 g, 0.08 mmoles) and DMF (0.5 ml). Purification was achieved by column chromatography (silica, toluene : 10 % EtOAc) and the band at $R_f = 0.8$ collected. Evaporation to dryness was performed under reduced pressure to afford pure *[G-3]-Pn* as a yellow oil; (0.085 g, 79 % yield); IR (evaporated film) 2963.5, 2232.5, 1616.6, 1485.3, 1262, 1094.5 cm^{-1}; Found C, 79.08 %; H, 5.38 %; N, 1.46 %; $C_{113}H_{94}O_{15}N_2$ requires C, 78.91 %; H, 5.51 %; N, 1.63 %; δ_H (500 MHz, $CDCl_3$) 4.97 (8H, s), 5.03 (16H, s), 5.05 (2H, s), 6.60-6.63 (7H, brm), 6.69 (2H, d), 6.71-6.74 (12H, brm), 7.10 (1H, dd), 7.23 (1H, d), 7.29-7.46 (40H, m), 7.54 (1H, d); MS (FAB) *m/e* 1720, (M^+) requires 1720.

4.5.4 Synthesis of *4-(2'-(3'',5''-dibenzyloxy)benzyloxyethyloxy) phthalonitrile* (4)

A solution of 2-(3',5'-dibenzyloxy)benzyloxyethanol (0.5 g, 1.4 mmoles) and 4-nitrophthalonitrile (0.3 g, 1.7 mmoles) in dry DMSO (20 ml) was added to potassium carbonate (0.24 g, 1.7 mmoles) under a nitrogen

atmosphere. The reaction mixture was heated at 60 °C for 48 hours, after which time TLC analysis (DCM) indicated no starting alcohol remained. The mixture was poured into water (100 ml) and the aqueous layer extracted with toluene (3x 30 ml). The combined organic extracts were washed with aqueous NaCl (50 ml), dried over magnesium sulphate and the solvent evaporated under reduced pressure to afford a thick yellow oil. Purification was achieved by column chromatography (silica, 10 % diethyl ether : toluene) and the band at $R_f = 0.6$ collected. Evaporation to dryness was performed under reduced pressure to afford the product as a clear oil which crystallised from a dichloromethane : petrol solution (4 : 1) to afford *4-(2'-(3'',5''-dibenzyloxy)benzyloxyethyloxy) phthalonitrile* as white needles; (0.62 g, 90 % yield); m.p. 112-113 °C; IR (KBr disc) 2932.6, 2228.2, 1596.5, 1497.3, 1147.0 cm^{-1}; Found C, 75.88 %; H, 5.26 %; N, 5.59 %; $C_{31}H_{26}O_4N_2$ requires C, 75.90 %; H, 5.34 %; N, 5.71 %; δ_H (200 MHz, $CDCl_3$) 3.82 (2H, t,), 4.20 (2H, t), 4.56 (2H, s), 5.05 (4H, s), 6.59 (3H, brs), 7.20 (1H, dd), 7.28 (1H, d), 7.40 (10H, m), 7.67 (1H, d); MS (CI) *m/e* 508, $(MNH_4)^+$ requires 508.

4.5.5 Synthesis of *4-(2'-(3'',5''-di(3''',5'''-dibenzyloxy)benzyloxy) benzyloxyethyloxy) phthalonitrile* (5)

The procedure was the same as that described for the synthesis of 4-(2'-(3'',5''-dibenzyloxy)benzyloxyethyloxy) phthalonitrile using 2-(3',5'-di (3'',5''-dibenzyloxy)benzyloxy)benzyloxy ethanol (0.78 g, 1.0 mmoles), 4-nitrophthalonitrile (0.2 g, 1.2 mmoles), potassium carbonate (0.17 g, 1.2 mmoles) and dry DMSO (20 ml). Purification was achieved by column chromatography (silica, toluene) and the band at $R_f = 0.7$ collected. Evaporation to dryness under reduced pressure afford followed by

crystallisation and recrystallisation from EtOAc : hexane (3 : 1), afforded pure *4-(2'-(3'',5''-di(3''',5'''-dibenzyloxy)benzyloxy)benzyloxyethyloxy) phthalonitrile* as white cubes; (0.78 g, 85 % yield); m.p. 106-108 °C; IR (KBr disc) 2929.5, 2233.2, 1596.5, 1498.2, 1156.0 cm^{-1}; Found C, 77.34 %; H, 5.46 %; N, 3.02 %; $C_{59}H_{50}O_8N_2$ requires C, 77.44 %; H, 5.51 %; N, 3.06 %; δ_H (500 MHz, $CDCl_3$) 3.77 (2H, t,), 4.13 (2H, t), 4.54 (2H, s), 4.98 (4H, s), 5.03 (8H, s), 6.51 (1H, t), 6.57 (2H, t), 6.59 (2H, d), 6.68 (4H, d), 7.16 (1H, dd), 7.24 (1H, d), 7.35-7.45 (20H, m), 7.60 (1H, d); MS (EI/CI) *m/e* 933, $(MNH_4)^+$ requires 933.

4.5.6 Synthesis of *4-(4',4'-bis(4''-benzyloxyphenyl)pentyloxy) phthalonitrile* (6)

To a stirred solution of 4,4-bis(4'-benzyloxyphenyl) pent-1-ol[7] (10 g, 22 mmoles) and 4-nitrophthalonitrile (3.1 g, 18 mmoles) in dry DMSO (50 ml) at 60 °C under a nitrogen atmosphere was added anhydrous potassium carbonate (3.0 g, 22 mmoles). Heating and stirring was continued for 72 hours, after which time TLC analysis ($CHCl_3$), indicated no further 4-nitrophthalonitrile remained. The reaction mixture was cooled, poured into water (400 ml) and the aqueous layer extracted with toluene (3x 50 ml). The combined organic extracts were washed with water (2x 50 ml), dried over magnesium sulphate and evaporated to dryness under reduced pressure. Purification was achieved by column chromatography (silica, 50 % hexane : $CHCl_3$) with the band at $R_f = 0.5$ collected. Evaporation to dryness was performed under reduced pressure to afford pure *4-(4',4'-bis(4''-benzyloxyphenyl)pentyloxy) phthalonitrile* as a thick colourless oil (7.6 g, 73 % yield); IR (KBr disc) 2930.7, 2225.8, 1596.5, 1498.6, 1158.0 cm^{-1}; Found C, 81.00 %; H, 6.02 %; N, 4.79 %; $C_{39}H_{34}O_3N_2$

requires C, 80.94%; H, 5.92 %; N, 4.84 %; δ_H (200 MHz, $CDCl_3$) 1.65 (3H, s), 2.05 (2H, m), 2.28 (2H, m), 4.17 (2H, t), 5.08 (4H, s), 6.92 (4H, d), 7.16 (4H, d), 7.40 (11H, brm), 7.55 (1H, d), 7.92 (1H, d); MS (CI) *m/e* 596, $(MNH_4)^+$ requires 596.

4.5.7 Attempted synthesis of *4-bis(4'-(3'',5''-dibenzyloxy) benzyloxyphenyl) phthalonitrile* (7)

The procedure was the same as that described for the synthesis of 4-(4',4'-bis(4''-benzyloxyphenyl)pentyloxy) phthalonitrile using 4,4-bis(4'-(3'',5''-dibenzyloxy)benzyloxyphenyl) pent-1-ol (1.5 g, 1.5 mmoles), 4-nitrophthalonitrile (0.34 g, 1.9 mmoles), anhydrous potassium carbonate (0.27 g, 1.9 mmoles) and DMF (5 ml). Purification was achieved by column chromatography (silica, 75 % petroleum ether : toluene) and the band at $R_f = 0.6$ collected. Evaporation to dryness was performed under reduced pressure but afforded only 4-nitrophthalonitrile and the starting alcohol as indicated by δ_H NMR and FAB MS.

4.5.8 Synthesis of *6-(3',5'-dibenzyloxybenzyloxy)-2,3-naphthalonitrile ([G-1]-NPn)* (8)

[G-1]-OH (2 g, 6.25 mmoles), 6-hydroxy-2,3-naphthalonitrile (1.1 g, 5.67 mmoles)[8] and DCCI (1.12 g, 6.25 mmoles) were heated and stirred at 80 °C under a nitrogen atmosphere for 48 hours, after which time TLC analysis (DCM) indicated no 6-hydroxy-2,3-naphthalonitrile was present. Purification was achieved by column chromatography (silica, DCM) and the band at $R_f = 0.5$ collected. Evaporation to dryness was performed under reduced pressure to afford the crude product, which was further

recrystallised from DCM : petroleum ether (4 : 1), to afford the pure *6-(3',5'-dibenzyloxybenzyloxy)-2,3-naphthalonitrile* as a yellow powdery solid; (1.42 g, 50.3 % yield); m.p. 169-170 °C; IR (KBr disc) 2986.0, 2231.5, 1598.5, 1498.2, 1148.0 cm^{-1}; Found C, 80.01 %; H, 4.68 %; N, 5.57 %; $C_{33}H_{24}O_3N_2$ requires C, 79.82 %; H, 4.87 %; N, 5.64 %; δ_H (500 MHz, $CDCl_3$) 5.01 (4H, s), 5.18 (2H, s), 6.62 (1H, t), 6.70 (2H, d), 7.20 (1H, d), 7.30-7.50 (11H, m), 7.85 (1H, d), 8.20 (2H, d); MS (CI) *m/e* 514, $(MNH_4)^+$ requires 514.

4.6 Synthesis of Tetra-Substituted Phthalocyanines

4.6.1 Synthesis of *tetra [G-1]-phthalocyanine* (9)

To pentanol (2 ml) at 120 °C was added a small piece of lithium metal (5 mg, 0.7 mmoles). This was allowed to react and [G-1]-phthalonitrile (0.2 g, 0.45 mmoles) was then added. The reaction mixture was heated at 120 °C for 24 hours. 0.1 M acetic acid (0.5 ml) was added and stirred for a further hour at room temperature. Water (10 ml) was added and the reaction mixture evaporated to dryness under reduced pressure. The crude product was recrystallised from MeOH to afford a green crystalline solid, which was purified by flash column chromatography (silica, MeOH, toluene) and the band at $R_f = 0.45$ collected. Evaporation to dryness was performed under reduced pressure to afford the crude phthalocyanine which was reprecipitated into stirred MeOH from DCM (minimum amount). The precipitate was collected by centrifugation and the product dried overnight in a vacuum oven (0.1 mm Hg, 100 °C). Pure *tetra-[G-1]-phthalocyanine* was obtained as a dark blue crystalline solid; (0.143 g, 18.0 % yield); m.p. 115 °C to mesophase with isotropic phase 270 °C; IR (KBr disc) 3275.0, 2958.0, 2930.2, 1727.0, 1599.2, 1458.8, 1379.4, 1156.6,

1070.0 cm^{-1}; Found C, 78.30 %; H, 5.10 %; N, 6.20 %; $C_{119}H_{90}O_{12}N_8$ requires C, 77.92 %; H, 5.07 %; N, 6.27 %; UV/vis (toluene, λ_{max} (nm)) 718, 682, 654, 620, 422, 346; δ_H (500 MHz, $CDCl_3$, 60 °C) -3.2 (2H, s), 5.04 (16H, s), 5.06 (8H, s), 6.65 (4H, t), 6.75 (8H, d), 7.29-7.45 (40H, m), 7.60-9.20 (12H, brm); MS (FAB) *m/e* 1788, (M^+) requires 1788.

4.6.2 Synthesis of *tetra [G-2]-phthalocyanine* (10)

The procedure was the same as that described for the synthesis of tetra [G-1]-phthalocyanine using pentanol (1 ml), [G-2]-phthalonitrile (400 mg, 0.37 mmoles). Purification was achieved by flash column chromatography (silica, MeOH, toluene : 5 % EtOAc) and the band at R_f = 0.4 collected. Evaporation to dryness was performed under reduced pressure to afford the crude phthalocyanine, which was reprecipitated into stirred MeOH from DCM (minimum amount), centrifuged and dried in a vacuum oven overnight (0.1 mm Hg, 100 °C), to afford pure *[G-2]-phthalocyanine* as a blue crystalline solid; (0.086 g, 21.5 % yield); δ_H (500 MHz, $CDCl_3$, 60 °C) 1.0 (2H, brs), 4.98-5.08 (48H, brm), 5.51 (8H, s), 6.60-6.65 (12H, brt), 6.75-7.05 (24H, brd), 7.29-7.45 (80H, m), 7.60-9.20 (12H, brm). Spectrum broadened due to aggregation.

4.6.3 Synthesis of *tetra [G-3]-phthalocyanine* (11)

The procedure was the same as that described for the synthesis of tetra [G-1]-phthalocyanine using pentanol (1 ml), [G-2]-phthalonitrile (210 mg, 0.012 mmoles). Purification was achieved by flash column chromatography (silica, MeOH, toluene : 5 % EtOAc) and the band at R_f = 0.45 collected. Evaporation to dryness was performed under reduced

pressure to afford the crude phthalocyanine, which was reprecipitated into stirred MeOH from DCM (minimum amount), centrifuged and dried in a vacuum oven overnight (0.1 mm Hg, 100 °C), to afford pure *[G-3]-phthalocyanine* as a blue crystalline solid; (0.03 g, 3.5 % yield); δ_H (500 MHz, $CDCl_3$, 60 °C) 4.84-5.06 (120H, brm), 6.45-6.60 (28H, brm), 6.70-6.98 (56H, brm), 7.20-7.45 (160H, brm), 8.50-9.50 (12H, brm). Spectrum broadened due to aggregation.

4.6.4 Synthesis of *4-(2'-(3'',5''-dibenzyloxy)benzyloxyethyloxy) phthalocyanine* (12)

The procedure was the same as that described for the synthesis of tetra [G-1]-phthalocyanine using pentanol (5 ml), 4-(2'-(3'',5''-dibenzyloxy) benzyloxyethyloxy) phthalonitrile (0.15 g, 0.3 mmoles). Purification was achieved by column chromatography (silica, hot toluene : 10 % EtOH) and the band at R_f = 0.3 collected, followed by further purification by flash column chromatography (silica, MeOH) and the phthalocyanine removed with DCM (100 ml). The crude phthalocyanine was precipitated into EtOH from DCM (minimum amount) and isolated by centrifugation to afford pure *4-(2'-(3'',5''-dibenzyloxy)benzyloxyethyloxy) phthalocyanine* as a blue powder; (0.06 g, 40 % yield); m.p. 106-107 °C; IR (KBr disc) 3276.1, 2957.8, 2931.2, 1728.0, 1598.8, 1459.2, 1379.1, 1157.1, 1070.0 cm^{-1}; Found C, 76.07 %; H, 5.44 %; N, 5.80 %; $C_{124}H_{106}O_{16}N_8$ requires C, 75.82 %; H, 5.44 %; N, 5.71 %; UV/vis (toluene, λ_{max} (nm)) 722, 680, 654, 622, 420, 342; δ_H (500 MHz, $CDCl_3$, 60 °C) -3.20 (2H, brs), 4.11 (4H, t), 4.17 (4H, t), 4.53 (4H, m), 4.62 (4H, m), 4.78 (4H, s), 4.82 (4H, s), 5.06 (8H, s), 5.08 (8H, s), 6.63 (4H, m), 6.83 (4H, d), 6.85 (4H, d), 7.30-7.40 (40H, brm), 7.52 (4H, brm), 8.20 (4H, brm), 8.70 (4H, brm); MS (FAB) *m/e* 1965, $(MH)^+$

requires 1965.

4.6.5 Synthesis of *4-(2'-(3'',5''-di(3''',5'''-dibenzyloxy)benzyloxy) benzyloxyethyloxy) phthalocyanine* (13)

The procedure was the same as that described for the synthesis of tetra [G-1]-phthalocyanine using pentanol (5 ml) and 4-(2'-(3'',5''-di(3''',5'''-dibenzyloxy)benzyloxy)benzyloxyethyloxy) phthalonitrile (0.4 g, 0.43 mmoles). Purification was achieved by column chromatography (silica, hot toluene : 10 % EtOH) and the band at R_f = 0.4 collected, followed by further purification by flash column chromatography (silica, MeOH) and the phthalocyanine removed with DCM (100 ml). The crude phthalocyanine was precipitated into EtOH from DCM (minimum amount) and isolated by centrifugation. Subsequent drying under vacuum (0.1 mm Hg, 125 °C) afforded the product as a blue solid; (0.15 g, 37 % yield); m.p. 95-96 °C; IR (KBr disc) 3277.0, 2922.9, 2854.6, 1726.9, 1595.8, 1460.2, 1156.0 cm^{-1}; Found C, 77.42 %; H, 5.71 %; N, 3.31 %; $C_{236}H_{202}O_{32}N_8$ requires C, 77.40 %; H, 5.56 %; N, 3.06 %; UV/vis (toluene, λ_{max} (nm)) 724, 682, 650, 624, 424, 340 cm; δ_H (500 MHz, $CDCl_3$, 60 °C) -2.2 (2H, brs), 4.16 (8H, m), 4.67 (8H, m), 4.90 (56H, brm), 6.41 (8H, brm), 6.57 (20H, brm), 6.82 (8H, brm), 7.29 (80H, brm), 7.65 (4H, brm), 8.55 (4H, brm), 8.98 (4H, brm); MS (FAB) *m/e* 3662, (M^+) requires 3662.

4.6.6 Synthesis of *tetra (4',4'-bis(4''-benzyloxyphenyl)pentyloxy) phthalocyanine* (14)

The procedure was the same as that described for the synthesis of tetra [G-1]-phthalocyanine using pentanol (2 ml) and 4-(4',4'-bis(4''-

benzyloxyphenyl)pentyloxy) phthalonitrile (0.3 g, 0.52 mmoles). Purification was achieved by column chromatography (silica, MeOH, DCM) and the band at $R_f = 0.35$ collected. The crude phthalocyanine was precipitated into EtOH from DCM (minimum amount) and isolated by centrifugation. Subsequent drying under vacuum (0.1 mm Hg, 125 °C) afforded tetra *(4',4'-bis(4''-benzyloxyphenyl)pentyloxy) phthalocyanine* as a green solid; (0.026 g, 9.0 % yield); m.p. 120-121 °C; IR (KBr disc) 2928.3, 2853.2, 1597.4, 1496.5, 1158.7 cm^{-1}; Found C, 80.95 %; H, 6.12 %; N, 5.08 %; $C_{156}H_{138}O_{12}N_8$ requires C, 80.87 %; H, 6.00 %; N, 4.84 %; UV/vis (toluene, λ_{max} (nm)) 726, 680, 650, 624, 418, 342; δ_H (500 MHz, $CDCl_3$, 60 °C) -2.60 (2H, brs), 1.84 (6H, s), 1.88 (6H, s), 1.89 (4H, brm), 2.02 (4H, brm), 2.44 (4H, brm), 2.38 (4H, brm), 3.95 (4H, brm), 4.21 (4H, brm), 4.92 (8H, s), 4.94 (8H, s), 7.10-7.50 (72H, brm), 7.60 (4H, m), 8.50 (4H, brm), 9.08 (4H, brm); MS (FAB) *m/e* 2316, (M^+) requires 2316.

4.6.7 Synthesis of *tetra-[G-1]-naphthalocyanine* (15)

The procedure was the same as that described for the synthesis of tetra [G-1]-phthalocyanine using pentanol (5 ml), [G-1]-naphthalonitrile (0.2 g, 0.04 mmoles). Purification was achieved by column chromatography (silica, MeOH, DCM) and the band at $R_f = 0.45$ collected. The crude naphthalocyanine was precipitated into MeOH from DCM (minimum amount) and isolated by centrifugation. Subsequent drying under vacuum (0.1 mm Hg, 125 °C) afforded pure *tetra [G-1]-naphthalocyanine* as a dark blue crystalline solid; (0.36 g, 4.5 % yield) m.p. 126.8 °C; IR (KBr disc) 3288.0, 1612.2, 1501.2, 1449.8, 1380.8, 1154.5, 1019.1 cm^{-1}; Found C, 79.54 %; H, 5.54 %; N, 5.12 %; $C_{132}H_{98}O_{12}N_8$ requires C, 79.74 %; H, 4.97 %; N, 5.64 %; UV/vis (solid, λ_{max} (nm)) 704, 658, 630, 362,

(toluene, λ_{max} (nm) 698, 322, 290; δ_H (500 MHz, $CDCl_3$, 60 °C) featureless and inconclusive; MS (FAB) found *m/e* 1988, (M^+) requires 1988.

4.7 Synthesis of Di-Bromides

4.7.1 Synthesis of *di-bromo catechol* [9] (16)

To an ice cooled solution of catechol (15 g, 136 mmoles) in DCM (200 ml) was added dropwise a solution of bromine (15 ml, 291 mmoles) in DCM (50 ml). The reaction mixture was stirred at room temperature for 2 hours, after which time the product precipitated out of solution. The reaction mixture was filtered and the precipitate recrystallised from water to afford pure *di-bromo catechol* as brown needle like crystals; (32g, 87 % yield); m.p. 92 °C.

4.7.2 Synthesis of *1,2-dibromo-4,5-bis(3',5' dibenzyloxy) benzyloxybenzene* (17)

4,5-Dibromocatechol (1.0 g, 3.73 mmoles) and [G-1]-OH (2.62 g, 8.18 mmoles) were dried by adding a small amount of toluene and distilling off the resultant azeotropic mixture. DCCI[6] (1.7 g, 8.2 mmoles) was added and the reaction stirred at 80 °C under a nitrogen atmosphere for 48 hours until TLC analysis (toluene : 5% EtOAc) indicated no starting dibromo catechol remained. Purification was achieved by column chromatography (toluene) and the band at $R_f = 0.5$ collected. Evaporation to dryness was performed under reduced pressure to afford pure *1,2-dibromo-4,5-bis(3',5'-dibenzyloxy)benzyloxy benzene* as a white crystalline solid; (2.9 g, 92.3 % yield); m.p. 104-106 °C; IR (KBr disc) 3031.4, 2927.7,

2869.0, 1597.5, 1493.9, 1451.3, 1375.5, 1156.1, 1059 cm^{-1}; Found C, 66.05 %; H, 4.73 %; Br, 18.30 %; $C_{48}H_{40}O_6Br_2$ requires C, 66.06 %; H, 4.73 %; Br, 18.31 %; δ_H (500 MHz, $CDCl_3$) 4.91 (8H, s), 5.02 (4H, s), 6.49 (2H, t), 6.64 (4H, d), 7.09 (2H, s), 7.25-7.34 (20H, brm); MS (FAB) found *m/e* 868/872 (ca. 1:1), (M^+) requires 868/872.

4.7.3 Synthesis of *1,2-dibromo-4,5-bis(3',5'-di(3'',5''-dibenzyloxy) benzyloxy)benzyloxy benzene* (18)

The procedure was the same as that described for the synthesis of 1,2-dibromo-4,5-bis(3',5'-dibenzyloxy)benzyloxy benzene using 4,5-dibromocatechol (0.82 g, 3.06 mmoles), [G-2]-OH (5.0 g, 6.72 mmoles) and DCCI[6] (1.41 g, 6.83 mmoles). Purification was achieved by column chromatography (silica, DCM) and the band at $R_f = 0.5$ collected. Evaporation to dryness was performed under reduced pressure to afford pure *1,2-dibromo-4,5-bis(3',5'-di(3'',5''-dibenzyloxy)benzyloxy)benzyloxy benzene* as an expanded foam; (3.63 g, 68.9 % yield); IR (KBr disc) 3031.2, 2928.4, 2871.8, 1596.8, 1495.6, 1451.3, 1376.2, 1157.0, 1056.1 cm^{-1}; Found C, 72.64 %; H, 5.24 %; Br, 9.12 %; $C_{104}H_{88}O_{14}Br_2$ requires C, 72.56 %; H, 5.15 %; Br, 9.28 %; δ_H (500 MHz, $CDCl_3$) 4.90 (8H, s), 5.00 (16H, s), 5.12 (4H, s), 6.52 (2H, t), 6.56 (4H, t), 6.65 (8H, d), 6.77 (4H, d), 7.16 (2H, s), 7.25-7.40 (40H, brm); MS (FAB) found *m/e* 1718/1722 (ca. 1:1), (M^+) requires 1718/1722.

4.7.4 Synthesis of *1,2-dibromo-4,5-(4',4'-bis(4''-benzyloxyphenyl) pentyloxy) benzene* (19)

The procedure was the same as that described for the synthesis of 1,2-

dibromo-4,5-bis(3',5'-dibenzyloxy)benzyloxybenzene using 4,5-dibromocatechol (0.5 g, 1.87 mmoles), 4,4-bis(4'-(3'',5''-dibenzyloxy) benzyloxyphenyl) pent-1-ol[7] (1.9 g, 1.67 mmoles) and DCCI[6] (0.85 g, 4.1 mmoles). Purification was achieved by column chromatography (silica, toluene : 25 % petroleum ether) and the band at $R_f = 0.5$ collected. Evaporation to dryness, under reduced pressure, yielded *1,2-dibromo-4,5-(4',4'-bis(4''-benzyloxyphenyl)pentyloxy) benzene* as a yellow oil; (4.4 g, 92.2 % yield); IR (evaporated film) 2950.0, 1685.4, 1597.4, 1397.3, 1250.7, 1025.2 cm^{-1}; Found C, 71.66 %; H, 5.66 %; N, 14.11 %; $C_{68}H_{64}O_6Br_2$ requires C, 71.83 %; H, 5.67 %; N, 14.05 %; δ_H (500 MHz, $CDCl_3$) 1.66 (6H, s), 1.69 (4H, m), 3.94 (4H, t), 5.05 (8H, s), 6.92 (8H, d), 7.06 (2H, s), 7.18 (8H, d), 7.37-7.53 (20H, brm); MS (FAB) found *m/e* 1134/1138 (ca. 1:1), (M^+) requires 1134/1138.

4.7.5 Synthesis of *1,2-dibromo-4,5-(4',4'-bis(4''-(3''',5'''-dibenzyloxy) benzyloxyphenyl)pentyloxy) benzene* (20)

The procedure was the same as that described for the synthesis of 1,2-dibromo-4,5-bis(3',5'-dibenzyloxy)benzyloxy benzene using dibromo catechol (0.2 g, 0.75 mmoles), [G-1]-OH (1.5 g, 4.69 mmoles) and DCCI[6] (0.34 g, 1.65 mmoles). Purification was achieved by column chromatography (silica, DCM) and the band at $R_f = 0.5$ collected. Evaporation to dryness was performed under reduced pressure to afford pure *1,2-dibromo-4,5-(4',4'-bis(4''-(3''',5'''-dibenzyloxy)benzyloxyphenyl) pentyloxy) benzene* as a brown oil; (0.61 g, 40 % yield); IR (evaporated film) 2925.8, 2870.0, 1597.5, 1507.1, 1452.2, 1397.2, 1247.2, 1156.2, 1024.6 cm^{-1}; Found C, 73.75 %; H, 5.05 %; Br, 8.05 %; $C_{124}H_{114}O_{14}Br_2$ requires C, 74.92 %; H, 5.78 %; Br, 8.03 %; δ_H (200 MHz, $CDCl_3$) 1.3 (4H, m),

1.55-1.65 (8H, brs), 2.20 (4H, m), 3.90 (4H, t), 4.90 (8H, s), 5.00 (16H, s), 6.60 (4H, t), 6.70 (8H, t), 6.85 (8H, d), 7.00 (2H, s), 7.12 (8H, d), 7.25-7.50 (20H, brm); MS (FAB) found *m/e* 2007/2011 (ca. 1:1), $(MNa)^+$ requires 2007/2011.

4.8 Synthesis of 4,5-Di-Substituted Phthalonitriles

4.8.1 Synthesis of *4,5-bis(3',5'-dibenzyloxy)benzyloxy phthalonitrile* (21)

To 1,2-dibromo-4,5-bis(3',5'-dibenzyloxy)benzyloxy benzene (1.0 g, 1.17 mmoles) and DMF (10 ml) was added Cu(I)CN[10] (0.315 g, 3.52 mmoles). The reaction mixture was heated to 140 °C and stirred overnight under a nitrogen atmosphere. The reaction mixture was poured into ammonia solution (200 ml) and stirred for 30 minutes, after which time it was filtered and the resultant green solid isolated. Purification was achieved by column chromatography (silica, 50 % toluene : 50 % DCM) and the band at $R_f = 0.6$ collected. Evaporation to dryness was performed under reduced pressure to afford *4,5-bis(3',5'-dibenzyloxy)benzyloxy phthalonitrile* as a white crystalline solid; (0.62 g, 71 % yield); m.p. 109-111 °C; IR (KBr disc) 3030.0, 2879.4, 2227.2, 1598.3, 1497.6, 1451.0, 1363.9, 1149.3, 1089.5 cm^{-1}; Found C, 78.80 %; H, 5.19 %; N, 3.42 %; $C_{50}H_{40}O_6N_2$ requires C, 78.52 %; H, 5.27 %; N, 3.66 %; δ_H (200 MHz, $CDCl_3$) 4.95 (8H, s), 5.15 (4H, s), 6.56 (2H, t), 6.62 (4H, d), 7.10 (2H, s), 7.29-7.40 (20H, brm); MS (FAB) found *m/e* 787, $(MNa)^+$ requires 787.

4.8.2 Synthesis of *4,5-bis(3',5'-di(3'',5''-dibenzyloxy)benzyloxy) benzyloxy phthalonitrile* (22)

The procedure was the same as that described for the synthesis of 1,2-dibromo-4,5-bis(3',5'-di(3'',5''-dibenzyloxy)benzyloxy)benzyloxybenzene (1.0 g, 1.34 mmoles), DMF (10 ml) and Cu(I)CN[10] (0.16 g, 1.78 mmoles). Purification was achieved by column chromatography (silica, DCM) and the band at $R_f = 0.7$ collected. Evaporation to dryness was performed under reduced pressure to afford pure *4,5-bis(3',5'-di(3'',5''-dibenzyloxy) benzyloxy)benzyloxy phthalonitrile* as a yellow oil; (0.68 g, 36 % yield); IR (evaporated film) 3032, 2928, 2873, 2228, 1598, 1497, 1453, 1376, 1154, 1055 cm^{-1}; Found C, 79.11 %; H, 5.61 %; N, 1.43 %; $C_{106}H_{88}O_{14}N_2$ requires C, 78.89 %; H, 5.50 %; N, 1.74 %; δ_H (200 MHz, $CDCl_3$) 4.90 (8H, s), 5.05 (16H, s), 5.08 (4H, s), 6.60 (6H, t), 6.68 (12H, d), 7.20 (2H, s), 7.29-7.48 (40H, brm); MS (FAB) found *m/e* 1636, $(MNa)^+$ requires 1636.

4.8.3 Synthesis of *4,5-bis(4',4'-bis(4''-benzyloxyphenyl)pentyloxy) phthalonitrile* (23)

The procedure was the same as that described for the synthesis of 1,2-dibromo-4,5-(4',4'-bis(4''-benzyloxyphenyl)pentyloxy) benzene (1.0 g, 0.88 mmoles), DMF (10 ml) and Cu(I)CN[10] (0.32 g, 3.52 mmoles). Purification was achieved by column chromatography (silica, toluene) and the band at $R_f = 0.7$ collected. Evaporation to dryness was performed under reduced pressure to afford pure *4,5-bis(4',4'-bis(4''-benzyloxyphenyl) pentyloxy) phthalonitrile* as a white crystalline solid; (0.62 g, 71 % yield); m.p. 111-112 °C; IR (KBr disc) 3032.5, 2961.7, 2871.6, 2228.7, 1587.0, 1510.8, 1454.7, 1379.2, 1243.4, 1181.2, 1023.2 cm^{-1}; Found C, 81.48 %; H, 6.28 %; N, 2.75 %; $C_{70}H_{64}O_6N_2$ requires C, 81.68 %; H, 6.27 %; N, 2.72 %;

δ_H (500 MHz, $CDCl_3$) 1.60 (6H, s), 1.65-1.75 (4H, brm), 3.98 (4H, t), 5.00 (8H, s), 6.88 (8H, d), 7.13 (8H, d), 7.20-7.50 (22H, brm); MS (FAB) found *m/e* 1029, (M^+) requires 1029.

4.8.4 Synthesis of *4,5-(4',4'-bis(4''-(3''',5'''-dibenzyloxy) benzyloxyphenyl)pentyloxy) phthalonitrile* (24)

The procedure was the same as that described for the synthesis of 1,2-dibromo-4,5-(4',4'-bis(4''-(3''',5'''-dibenzyloxy)benzyloxyphenyl)pentyloxy) benzene (0.5 g, 0.25 mmoles), DMF (10 ml) and Cu(I)CN[10] (0.07 g, 0.78 mmoles). Purification was achieved by column chromatography (silica, DCM) and the band at $R_f = 0.7$ collected. Evaporation to dryness was performed under reduced pressure to afford pure *4,5-(4',4'-bis(4''-(3''',5'''-dibenzyloxy)benzyloxyphenyl)pentyloxy) phthalonitrile* as a yellow oil; (0.36 g, 76 % yield); IR (evaporated film) 3032.5, 2924.4, 2872.3, 2227.9, 1597.8, 1505.7, 1453.0, 1379.7, 1245.3, 1157.1 1059.7 cm^{-1}; Found C, 80.68 %; H, 5.99 %; N, 1.42 %; $C_{126}H_{112}O_{14}N_2$ requires C, 80.57 %; H, 6.01 %; N, 1.49 %; δ_H (200 MHz, $CDCl_3$) 1.3 (4H, m), 1.52-1.70 (8H, brs), 2.20 (4H, m), 3.90 (4H, t), 4.90 (8H, s), 5.00 (16H, s), 6.60 (4H, t), 6.70 (8H, t), 6.85 (8H, d), 7.00 (2H, s), 7.12 (8H, d), 7.25-7.50 (40H, brm); MS (FAB) found *m/e* 1878, (M^+) requires 1878.

4.9 Synthesis of Other Phthalonitrile Precursors

4.9.1 Synthesis of *1,2-dibromo-(4,5-bis(3',5'-dibenzyloxy) benzyloxymethyl) benzene* (25)

To a stirred solution of sodium hydride (0.1 g, 4.2 mmoles) in THF (10 ml),

was added [G-1]-OH (0.83 g, 2.6 mmoles) in THF (10 ml). After 30 minutes the mixture was added slowly via a dropping funnel to the 1,2-dibromo-4,5-bromomethylbenzene[11] (0.5 g, 1.19 mmoles). Stirring was continued overnight at room temperature and under a nitrogen atmosphere. The reaction mixture was then poured into water and extracted with DCM (3x 50 ml), dried over magnesium sulphate and evaporated to dryness under reduced pressure to yield crude *1,2-dibromo-(4,5-bis(3',5'-dibenzyloxy)benzyloxymethyl) benzene* as a white crystalline solid. Recrystallisation from toluene : hexane (3 : 1) afforded the pure product as white needle like crystals; (0.17 g, 15 % yield); m.p. 112-113 °C; IR (KBr disc) 2924.8, 2854.7, 1595.7, 1450.6, 1372.7, 1156.0, 1058.0 cm^{-1}; Found C, 66.82 %; H, 4.99 %; Br, 17.42 %; $C_{50}H_{44}O_6Br_2$ requires C, 66.68 %; H, 4.92 %; Br, 17.74 %; δ_H (200 MHz, $CDCl_3$) 4.62 (4H, s), 5.01 (4H, s), 5.03 (8H, s), 6.56 (1H, t), 6.62 (4H, d), 7.34 (2H, s), 7.35-7.48 (20H, m); MS (EI/CI) found *m/e* 914/918 (ca. 1:1), $(MNH_4)^+$ requires 914/918.

4.9.2 Synthesis of *1,2-dibromo-(4,5-bis(3',5'-di(3'',5''-dibenzyloxy) benzyloxy)benzyloxymethyl) benzene* (26)

The procedure was the same as that described for the synthesis of 1,2-dibromo-(4,5-bis(3',5'-dibenzyloxy) benzyloxymethyl) benzene using sodium hydride (0.1 g, 4.2 mmoles) in THF (10 ml) and [G-2]-OH (0.83 g, 1.1 mmoles) in THF (10 ml). After 30 minutes the mixture was added slowly via a dropping funnel to 1,2-dibromo-(4,5-dibromomethyl) benzene[11] (0.5 g, 1.19 mmoles). Recrystallisation from toluene/hexane afforded *1,2-dibromo-(4,5-bis(3',5'-di(3'',5''-dibenzyloxy)benzyloxy) benzyloxymethyl) benzene* as white solid in trace amounts; IR (KBr disc) 2926.9, 2854.9, 1593.0, 1452.4, 1378.2, 1156.0, 1058.1 cm^{-1}.

4.9.3 Synthesis of *4,5-bis(3',5'-dibenzyloxy)benzyloxymethyl phthalonitrile* (27)

The procedure was the same as that described for the synthesis of 4,5-bis(3',5'-dibenzyloxy)benzyloxy phthalonitrile using 1,2-dibromo-(4,5-bis(3',5'-dibenzyloxy)benzyloxymethyl) benzene (0.16 g, 0.17 mmoles), DMF (20 ml) Cu (I) CN[10] (0.05 g, 0.56 mmoles). Purification was achieved by column chromatography (silica, 50 % DCM : 50 % toluene) and the band at R_f = 0.6 collected. A trace amount of copper octa-(3',5'-dibenzyloxy)benzyloxymethyl) phthalocyanine was also formed. Evaporation to dryness was performed under reduced pressure to afford a trace amount of *4,5-bis(3',5'-dibenzyloxy)benzyloxymethyl phthalonitrile;* IR (evaporated film) 3032.5, 2927.7, 2866.6, 2228.8, 1595.9, 1496.6, 1450.7, 1375.3, 1156.3, 1058.0 cm^{-1}.

4.10 Synthesis of Octa-Substituted Phthalocyanines

4.10.1 Synthesis of *octa [G-1]-phthalocyanine* (28)

The procedure was the same as that described for the synthesis of tetra [G-1] phthalocyanine using pentanol (2 ml) and 4,5-bis(3',5'-dibenzyloxy) benzyloxy phthalonitrile (0.1 g, 0.13 mmoles). Purification was achieved by column chromatography (silica, MeOH, toluene) and the band at R_f = 0.5 collected. The crude phthalocyanine was precipitated into MeOH from DCM (minimum amount) and isolated by centrifugation. Subsequent drying under vacuum (0.1 mm Hg, 125 °C) afforded pure *octa [G-1]-phthalocyanine* as a dark blue crystalline solid; (0.068 g, 17 % yield); m.p. 105 °C ; IR (KBr disc) 3415.5, 2925.0, 2855.5, 1599.0, 1494.0, 1445.8, 1372.6, 1151.3, 1022.5 cm^{-1}; Found C, 78.09 %; H, 5.47 %; N, 3.78 %;

$C_{200}H_{162}O_{24}N_8$ requires C, 78.46 %; H, 5.33 %; N, 3.66 %; UV/vis (toluene, λ_{max} (nm)) 720, 684, 638, 414, 342; δ_H (500 MHz, $CDCl_3$, 60 °C) -3.0 to -3.1(2H, brs), 4.81 (48H, brs), 6.60 (8H, t), 7.12-7.45 (96H, brm), 8.7-9.4 (8H, brm); MS (FAB) *m/e* 3062, (M^+) requires 3062.

4.10.2 Attempted synthesis of *octa [G-2] phthalocyanine* (29)

The synthesis of octa [G-2] phthalocyanine was attempted by the cyclotetramisation of 4,5-bis(3',5'-di(3'',5''-dibenzyloxy)benzyloxy) benzyloxy phthalonitrile. The resulting material did not resemble a phthalocyanine in appearance and analytical analysis proved inconclusive by all techniques investigated.

4.10.3 Synthesis of *copper containing octa-(3',5'-dibenzyloxy) benzyloxymethyl phthalocyanine* (30)

During the synthesis of bis(3',5'-dibenzyloxy)benzyloxymethyl)-phthalonitrile, small amounts of *copper containing octa-(3',5'-dibenzyloxy) benzyloxymethyl phthalocyanine* were formed; (0.005 g, 1 % yield, based on 100% conversion of phthalonitrile); IR (KBr disc) 3376.9, 2927.7, 2866.6, 1595.9, 1496.6, 1450.7, 1375.3, 1156.3, 1058.0 cm^{-1}; UV/vis (toluene, λ_{max} (nm)) 680, 656, 616, 486.

4.10.4 Synthesis of *octa-(4',4'-bis(4''-benzyloxyphenyl)pentyloxy) phthalocyanine* (31)

The procedure was the same as that described for the synthesis of tetra [G-1] phthalocyanine using pentanol (2 ml), 4,5-di-(4',4'-bis(4''-

benzyloxyphenyl)pentyloxy) phthalonitrile (0.2 g, 0.19 mmoles). Purification was achieved by column chromatography (silica, MeOH, acetone) and the band at $R_f = 0.4$ collected. The crude phthalocyanine was precipitated into MeOH from DCM (minimum amount) and isolated by centrifugation. Subsequent drying under vacuum (0.1 mm Hg, 125 °C) afforded pure *octa-(4',4'-bis(4''-benzyloxyphenyl)pentyloxy) phthalocyanine* as a dark blue crystalline solid; (0.011 g, 2.8 % yield); m.p. 98-100 °C; IR (KBr disc) 3412.4, 2926.2, 2858.5, 1601.2, 1499.8, 1444.5, 1371.6, 1149.6, 1023.3 cm^{-1}; Found C, 81.52 %; H, 6.02 %; N, 2.79 %; $C_{280}H_{258}O_{24}N_8$ requires C, 81.65 %; H, 6.31 %; N, 2.72 %; UV/vis (toluene, λ_{max} (nm)) 722, 680, 654, 618, 428, 340; δ_H (200 MHz, $CDCl_3$) -3.12 (2H, brs) 1.54 (24H, s), 1.25-1.31 (16H, brm), 2.01-2.07 (16H, brm), 3.46 (16H, t), 5.02 (32H, s), 6.87 (32H, s), 7.14 (32H, t), 7.25-7.45 (80H, m), 8.62-8.75 (8H, brm); MS (CI) *m/e* Spectrum unobtainable.

4.10.5 Synthesis of *octa-4,5-(4',4'-bis(4''-(3''',5'''-dibenzyloxy) benzyloxyphenyl)pentyloxy) phthalocyanine* (32)

The procedure was the same as that described for the synthesis of tetra [G-1] phthalocyanine using pentanol (2 ml) and 4,5-bis(3',5'-dibenzyloxy) benzyloxy phthalonitrile (0.05 g, 0.028 mmoles). The reaction was heated at 140 °C overnight after which time no traces of phthalocyanine were observed and it was concluded that cyclotetramisation had not taken place.

4.11 Synthesis of Non-Uniformly Substituted Phthalocyanines

4.11.1 Synthesis of *mono-[G-1] -hexa(diethyleneoxy) phthalocyanine* (33)

Lithium hydride (0.02 g, 0.54 mmoles) was added to a stirred solution of [G-1]-phthalonitrile (0.122 g, 0.027 mmoles) and 4,5-bis(1,4,7-trioxaoctyl) phthalonitrile (1g, 0.27 mmoles) in dry pentanol (2 ml) at 140 °C under a nitrogen atmosphere. After a few minutes the solution turned dark blue. Heating and stirring was maintained for 6 hours. Glacial acetic acid (0.25 ml) was carefully added and the reaction mixture allowed to cool. Purification was achieved by column chromatography (silica, DCM : 6 % EtOH) and the band at $R_f = 0.1$ collected. The resultant green solid was precipitated into petroleum ether from the minimum amount of DCM, separated by centrifugation and dried under vacuum (0.1 mm Hg, 100 °C) overnight to afford *2-(3',5'-dibenzyloxy)benzyloxy-9,10,16,17,23,24-hexa(1,4,7-trioxaoctyl) phthalocyanine* as a dark green powder; (0.216 g, 51.3 % yield); m.p. 120-121 °C; IR (KBr disc) 3433.3, 2924.6, 2868.2, 1601.0, 1501.2, 1448.7, 1383.9, 1155.3, 1099.0 cm^{-1}; Found C, 64.47 %; H, 6.32 %; N, 6.84 %; $C_{83}H_{96}O_{21}N_8$ requires C, 64.66 %; H, 6.23 %; N, 7.27 %; UV/vis (toluene, λ_{max} (nm)) 700, 664, 646, 398, 342; δ_H (500 MHz, $CDCl_3$, 60 °C) -2.14 (2H, brs), 3.47 (18H, s), 3.70 (12H, t), 3.95 (12H, t), 4.20 (12H, t), 4.74 (12H, t), 5.18 (4H, s), 5.53 (2H, s), 6.69 (1H, t), 7.05 (2H, d), 7.22-7.50 (10H, brm), 8.55-8.70 (8H, brm), 9.05 (1H, d); MS (FAB) *m/e* 1542, (M^+) requires 1542.

4.11.2 Synthesis of *di-[G-1]-hexa(diethyleneoxy) phthalocyanine* (34)

The procedure was the same as that described for the synthesis of 2-(3',5'-dibenzyloxy)benzyloxy-9,10,16,17,23,24-hexa(1,4,7-trioxaoctyl) phthalocyanine using lithium hydride (0.02 g, 0.54 mmoles), 4,5-bis(3',5'-dibenzyloxy)benzyloxy phthalonitrile (0.1 g, 0.014 mmoles), 4,5-bis(1,4,7-trioxaoctyl) phthalonitrile (0.5 g, 0.14 mmoles) and pentanol (2 ml). Purification was achieved by column chromatography (silica, DCM : 6 % EtOH) and the band at $R_f = 0.1$ collected. The resultant green solid was reprecipitated into petroleum ether from the minimum amount of DCM, separated by centrifugation and dried under vacuum (0.1 mm Hg, 100 °C) overnight to afford *2,3-bis((3',5'-dibenzyloxy)benzyloxy)-9,10,16,17,23,24-hexa(1,4,7-trioxaoctyl) phthalocyanine* as a dark green powder; (0.048 g, 19.7 % yield); m.p. 112-113 °C; IR (KBr disc) 3432.8, 2924.4, 2868.2, 1601.0, 1501.2, 1446.3, 1383.9, 1154.2, 1096.4 cm^{-1}; Found C, 64.01%; H, 6.65 %; N, 7.25 %; $C_{104}H_{114}O_{24}N_8$ requires C, 67.15 %; H, 6.18 %; N, 6.02 %; UV/vis (toluene, λ_{max} (nm)) 700, 664, 644, 406, 340; δ_H (500 MHz, $CDCl_3$, 60 °C) -2.14 (2H, brs), 3.47 (18H, s), 3.70 (12H, t), 3.95 (12H, t), 4.20 (12H, t), 4.74 (12H, t), 5.18 (4H, s), 5.55 (2H, s), 6.69 (1H, t), 7.05 (2H, d), 7.22-7.50 (10H, brm), 8.55-8.70 (8H, brm), 9.05 (1H, d); MS (FAB) *m/e* 1860, 1542 (ca. 1:1), (M^+) requires 1860.

4.11.3 Synthesis of *mono-[G-2] hexa(diethyleneoxy) phthalocyanine* (35)

The procedure was the same as that described for the synthesis of 2-(3',5'-dibenzyloxy)benzyloxy-9,10,16,17,23,24-hexa(1,4,7-trioxaoctyl) phthalocyanine using lithium hydride (0.02 g, 0.54 mmoles), [G-2]-phthalonitrile (0.12 g, 0.014 mmoles), 4,5-di(1,4,7-trioxaoctyl)

phthalonitrile (0.5 g, 0.14 mmoles) and pentanol (2 ml). Purification was achieved by column chromatography (silica, DCM : 5 % EtOH) and the band at R_f = 0.2 collected. The resultant green solid was reprecipitated into petroleum ether from the minimum amount of DCM, separated by centrifugation and dried under vacuum (0.1 mm Hg, 100 °C) overnight to afford *2-((3',5'-di(3'',5''-dibenzyloxy)benzyloxy)benzyloxy)-9,10,16,17,23,24-hexa(1,4,7-trioxaoctyl) phthalocyanine* as a dark blue powder; (0.089 g, 32.9 % yield); Tg 115.7 °C; IR (KBr disc) 3422.5, 2922.6, 2875.9, 1598.2, 1447.8, 1383.8, 1144.2, 1058.0 cm^{-1}; Found C, 67.99%; H, 6.45 %; N, 5.95 %; C_{111} H_{120} O_{25} N_8 requires C, 67.80 %; H, 6.15 %; N, 5.70 %; UV/vis (toluene, λ_{max} (nm)) 700, 664, 646, 404, 344; δ_H (500 MHz, $CDCl_3$, 60 °C) -2.18 to -1.84 (2H, brs), 3.46 (18H, s), 3.70 (12H, t), 3.95 (12H, t), 4.20 (12H, t), 4.74 (12H, t), 4.98 (8H, s), 5.10 (4H, s), 5.53 (2H, s), 6.60 (2H, t), 6.65 (1H, t), 6.73 (4H, d), 7.03 (2H, d), 7.18-7.32 (20H, brm), 8.52-8.70 (8H, brm), 9.02 (1H, d); MS (FAB) *m/e* 1989, $(MNa)^+$ requires 1989.

4.11.4 Synthesis of *di-[G-2] hexa(diethyleneoxy) phthalocyanine* (36)

The procedure was the same as that described for the synthesis of 2-(3',5'-dibenzyloxy)benzyloxy-9,10,16,17,23,24-hexa(1,4,7-trioxaoctyl) phthalocyanine using lithium hydride (0.02 g, 0.54 mmoles), 4,5-bis(3',5'-di(3'',5''-dibenzyloxy)benzyloxy)benzyloxy phthalonitrile (0.22 g, 0.14 mmoles), 4,5-di-(1,4,7-trioxaoctyl) phthalonitrile (0.5 g, 1.4 mmoles), pentanol (2 ml). Purification was achieved by column chromatography (silica, DCM : 5 % EtOH) and the band at R_f = 0.2 collected. The resultant green solid was reprecipitated into petroleum ether from the minimum amount of DCM, separated by centrifugation and dried under vacuum (0.1 mm Hg, 100 °C) overnight to afford *2,3-bis((3',5'-di(3'',5''-*

dibenzyloxy)benzyloxy)benzyloxy)-9,10,16,17,23,24-hexa(1,4,7-trioxaoctyl) phthalocyanine as a dark blue powder; (0.16 g, 43.3 % yield); Tg 93.5 °C; IR (KBr disc) 3424.8, 2923.4, 2876.3, 1596.2, 1446.5, 1382.5, 1138.1, 1055.0 cm^{-1}; Found C, 67.77%; H, 5.68 %; N, 4.82 %; $C_{160}H_{162}O_{32}N_8$ requires C, 71.94 %; H, 6.03 %; N, 4.14 %; UV/vis (toluene, λ_{max} (nm)) 700, 662, 648, 406, 340; δ_H (500 MHz, $CDCl_3$, 60 °C) -2.20 to -1.90 (2H, brs), 3.45 (18H, s), 3.70 (12H, t), 3.95 (12H, t), 4.20 (12H, t), 4.72-4.78 (12H, t), 4.96 (16H, s), 5.06 (8H, s), 5.60 (4H, s), 6.48 (4H, t), 6.52 (2H, t), 6.62 (8H, d), 7.08 (4H, d), 7.15-7.30 (40H, brm), 8.62-8.72 (8H, brd); MS (FAB) *m/e* 2732, 1989 $(MNa)^+$ requires 2732.

4.11.5 Synthesis of *mono-[G-3] hexa-(diethyleneoxy) phthalocyanine* (37)

The procedure was the same as that described for the synthesis of 2-(3',5'-dibenzyloxy)benzyloxy-9,10,16,17,23,24-hexa(1,4,7-trioxaoctyl) phthalocyanine using lithium hydride (0.02 g), [G-3]-phthalonitrile (0.24 g, 0.14 mmoles), 4,5-di(1,4,7-trioxaoctyl) phthalonitrile (0.5 g, 1.4 mmoles) and pentanol (2 ml). Purification was achieved by column chromatography (silica, DCM : 4 % EtOH) and the band at $R_f = 0.3$ collected. The resultant green solid was reprecipitated into petroleum ether from the minimum amount of DCM, separated by centrifugation and dried under vacuum (0.1 mm Hg, 100 °C) overnight to afford *2-((3',5'-di(3'',5''-di(3''',5'''-dibenzyloxy)benzyloxy)benzyloxy)benzyloxy)-9,10,16,17,23,24-hexa(1,4,7-trioxaoctyl)phthalocyanine* as a dark blue powder; (0.038 g, 8.9 % yield); Tg 103.4 °C; IR (KBr disc) 3428.6, 29224.2, 2876.0, 1598.8, 1446.3, 1385.0, 1138.2, 1055.7 cm^{-1}; Found C, 71.05 %; H, 6.08 %; N, 4.27 %; $C_{167}H_{168}O_{33}N_8$ requires C, 71.25 %; H, 6.02 %; N, 3.98 %;

UV/vis (toluene, λ_{max} (nm)) 702, 664, 640, 400, 340; δ_H (500 MHz, $CDCl_3$, 60 °C) -1.80 to -1.60 (2H, brs), 3.42 (18H, s), 3.70 (12H, t), 3.95 (12H, t), 4.20 (12H, t), 4.74 (12H, t), 4.88 (16H, s), 4.98 (8H, s), 5.06 (4H, s), 5.50 (2H, s), 6.48 (2H, t), 6.49 (1H, t), 6.52 (4H, t), 6.69 (8H, d), 6.72 (4H, d), 7.00 (2H, d), 7.15-7.35 (40H, brm), 8.52-8.72 (8H, brm), 9.05 (1H, d); MS (FAB) *m/e* 2815 (M^+) requires 2815.

4.12 Alternative Methods Of Phthalonitrile Cyclotetramerisation

4.12.1 Synthesis of *tetra [G-1] Zn-phthalocyanine* [12] (38)

A mixture of [G-1]-phthalonitrile (0.49 g, 1.1 mmoles) and zinc(II)acetate dihydrate (0.88 g, 4.0 mmoles) was heated at 200 °C for 4 hours. The resultant green compound was transferred to a short column of silica and washed with MeOH to remove impurities, then eluted with 10 % DCM : MeOH. Precipitation into MeOH from DCM, followed by centrifugation afforded *tetra [G-1] Zn-phthalocyanine* as a dark blue solid; (0.52 g, 25.5 % yield); m.p. 120 °C shows D_{hd} mesophase to isotropic at 200 °C; IR (KBr disc) 3372.7, 2918.9, 2869.4, 1601.3, 1487.4, 1449.7, 1334.6, 1153.4, 1046.9 cm^{-1}; Found C, 74.72 %; H, 4.94 %; N, 6.38 %; $C_{116}H_{88}O_{12}N_8Zn$ requires C, 75.26 %; H, 4.79 %; N, 6.05 %; UV/vis (toluene, λ_{max} (nm)) 682, 654, 622, 490, 350; δ_H (500 MHz, $CDCl_3$, 60 °C) 5.20 (8H, s), 5.21 (16H, s), 6.75 (4H, t), 7.06 (8H, d), 7.30-7.55 (40H, brm), 8.75-8.85 (8H, brm), 9.12 (4H, d); MS (FAB) *m/e* 1851, (M^+) requires 1851.

4.12.2 Synthesis of *tetra [G-1] Cu-phthalocyanine* [12] (39)

The procedure was the same as that described for the synthesis of tetra [G-1] Zn-phthalocyanine using, [G-1]-phthalonitrile (0.49 g, 1.1 mmoles) and copper(II)acetate dihydrate (0.80 g, 4.0 mmoles). Purification was achieved by column chromatography (silica, MeOH then 25 % DCM : MeOH) to afford trace amounts of *tetra [G-1] Cu-phthalocyanine* as a dark blue film; IR (KBr disc), elemental analysis, UV/vis (toluene), δ_H NMR (500 MHz, $CDCl_3$ at 60 °C) and MS (FAB) all proved inconclusive.

4.12.3 Synthesis of *tetra [G-2] Zn-phthalocyanine* [12] (40)

The procedure was the same as that described for the synthesis of tetra [G-1] Zn-phthalocyanine using, [G-2]-phthalonitrile (0.95 g, 1.1 mmoles) and zinc(II)acetate dihydrate (0.88 g, 4.0 mmoles). Purification was achieved by column chromatography (silica, MeOH then 5 % DCM : MeOH) to afford trace amounts of *tetra [G-2] Zn-phthalocyanine* as a dark blue film; IR (KBr disc), elemental analysis, UV/vis (toluene), δ_H NMR (500 MHz, $CDCl_3$ at 60 °C) and MS (FAB) all proved inconclusive.

4.12.4 Synthesis of *tetra [G-1] Zn-phthalocyanine* [13] (41)

[G-1]-phthalonitrile (0.59 g, 1.32 mmoles) was suspended in 10 ml of 2-dimethylaminoethanol (DMAE). The suspension was heated to 100 °C and a steady stream of ammonia gas passed into the solution for 2 hours. After this time, 1.5 ml of 1,8-diazatricyclo[5.4.0]undec-7-ene (DBU) was added, followed by zinc acetate (0.66 g, 3.0 mmoles) after 15 minutes. Ammonia gas was bubbled into the reaction mixture for a further 10 hours at 100-115 °C. The mixture was cooled to room temperature and 15

ml MeOH and 15 ml water added. TLC (toluene) and UV/vis indicated no phthalocyanine had formed after this time.

4.12.5 Synthesis of *[G-1]* substituted *(3,5 di-tertiary butyl -4-hydroxyphenyl) phthalocyanine* (42)

To tetra(3,5 di-*tertiary*-butyl-4-hydroxyphenyl) phthalocyanine (0.05 g, 0.04 mmoles) and [G-1]-Br (0.09 g, 0.23 mmoles) was added sodium hydride (0.05 g) and dry THF (20 ml). The reaction was stirred under an atmosphere of nitrogen at 40 °C for 6 days, by which time UV/vis analysis (toluene) indicated no starting phenol present when t-butyl ammonium hydroxide (1 ml) was added. Purification was achieved by column chromatography (silica, diethyl ether) and the band at $R_f = 0.6$ collected. The product was precipitated into MeOH from DCM (minimum amount), centrifuged and dried under vacuum (0.1 mm Hg, 100 °C) overnight to afford pure *tetra-[G-1] substituted (3,5 di-tertiary-butyl-4-hydroxyphenyl) phthalocyanine* as a dark green powder (0.021 g, 34.2 % yield); IR (KBr disc) 3416.6, 2923.8, 2858.1, 1595.3, 1497.7, 1452.7, 1375.5, 1159.2, 1059.2 cm^{-1}; Found C, 81.00 %; H, 6.40 %; N, 4.30 %; $C_{172}H_{170}O_{12}N_8$ requires C, 81.30 %; H, 6.70 %; N, 4.40 %; UV/vis (toluene, λ_{max} (nm)) 686, 620, 360, 286; δ_H (500 MHz, $CDCl_3$, 60 °C) -2.94 to -2.50 (2H, brs), 1.68 (72H, s), 4.86 (8H, s), 5.01 (16H, s), 6.30-6.80 (12H, bm), 7.28-7.45 (40H, brm), 8.18-8.32 (8H, bm), 9.60-10.02 (4H, bm); MS (FAB) *m/e* No spectrum was obtainable.

4.12.6 Synthesis of *[G-2]-substituted (3,5 di-tertiary-butyl-4-hydroxyphenyl) phthalocyanine* (43)

The procedure was the same as that described for the synthesis of the [G-1]-substituted tetra-(3,5-di-*tertiary*-butyl-4-hydroxyphenyl) phthalocyanine using tetra-(3,5 di-*tertiary*-butyl-4-hydroxyphenyl) phthalocyanine (0.05 g, 0.04 mmoles), [G-2]-Br (0.19 g, 0.23 mmoles), sodium hydride (0.05 g, 1.85 mmoles) and dry THF (20 ml). Purification was achieved by column chromatography (silica, diethyl ether) and the band at $R_f = 0.4$ collected. Evaporation to dryness was performed under reduced pressure to afford the product in trace amount only IR (KBr disc), elemental analysis, UV/vis (toluene), δ_H NMR (500 MHz, $CDCl_3$ at 60 °C) and MS (FAB) all proved inconclusive.

4.13 The Axial Substitution of Silicon Phthalocyanine with Dendritic Wedges

4.13.1 Preparation of *[G-1] axial substituted silicon phthalocyanine* (44)

To silicon phthalocyanine dichloride (0.2 g, 0.33 mmoles) and [G-1]-OH (0.42 g, 1.32 mmoles) was added sodium hydride (0.055 g, 2.3 mmoles). Toluene (2 ml) was added and the mixture was heated under nitrogen at 80 °C for 96 hours. After this time, TLC analysis (toluene : 5 % EtOAc) indicated no silicon phthalocyanine dichloride remained. The reaction mixture was poured into water and the aqueous layer extracted with toluene (3 x 50 ml), dried over magnesium sulphate and evaporated to dryness under reduced pressure. TLC analysis indicated the presence of mono and di axially substituted phthalocyanine. Purification was

achieved by column chromatography (silica, toluene) and the band at R_f = 0.5 collected. Further purification by flash column chromatography (silica, MeOH) isolated the crude phthalocyanine which was reprecipitated into stirred MeOH from DCM (minimum amount), centrifuged and dried in a vacuum oven overnight (0.1 mm Hg, 100 °C), to give pure *di((3',5'-dibenzyloxy)benzyloxy)phthalocyaninato silicon* as a blue prismatic crystals; (0.053 g, 14 % yield); m.p. 253 °C; Tg 139.1 °C ; IR (KBr disc) 3429.9, 2922.9, 2851.1, 1599.5, 1516.7, 1449.5, 1332.9, 1160.1, 1061.4 cm^{-1}; Found C, 75.37 %; H, 4.44 %; N, 9.56 %; $C_{74}H_{54}O_6N_8Si$ requires C, 75.36 %; H, 4.61 %; N, 9.50 %; UV/vis (solid, λ_{max} (nm)) 704, 658, 630, 362, (toluene, λ_{max} (nm)) 678, 650, 610, 354; δ_H (500 MHz, $CDCl_3$ 60 °C) -0.69 (4H, s), 3.58 (4H, d), 4.11 (8H, s), 5.64 (2H, t), 7.20-7.40 (20H, bm), 8.20-8.31 (8H, bm), 9.52-9.62 (8H, bm); MS (FAB) found *m/e* 1178, (M^+) requires 1178.

4.13.2 Preparation of *[G-2] axial substituted silicon phthalocyanine* (45)

The product was synthesised and purified as described for di((3',5'-dibenzyloxy)benzyloxy)phthalocyaninato silicon, and the band at R_f = 0.55 collected. Pure *di-((3',5'-di(3'',5''-dibenzyloxy)benzyloxy) benzyloxy)phthalocyaninato silicon* was obtained as a green prismatic crystals; (0.3 g, 45.2 %); m.p. 166 °C; Tg 124.4 °C; IR (KBr disc) 3436.2, 2923.5, 2892.6, 1597.6, 1519.2, 1451.5, 1333.5, 1148.4, 1067.3 cm^{-1}; Found C, 76.60 %; H, 4.82 %; N, 5.62 %; $C_{130}H_{102}O_{14}N_8Si$ requires C, 76.98 %; H, 5.07 %; N, 5.52 %; UV/vis (solid, λ_{max} (nm)) 692, 622, 354, (toluene, λ_{max} (nm)) 680, 650, 612, 348; δ_H (500 MHz, $CDCl_3$, 60 °C) -0.69 (4H, s), 3.54 (4H, d), 4.02 (8H, s), 4.96 (16H, s), 5.64 (2H, t), 6.32 (8H, d), 6.46 (4H, t),

7.20-7.40 (40H, bm), 8.20-8.31 (8H, brm), 9.52-9.62 (8H, m); MS (FAB) *m/e* 2028, $(MH)^+$ requires 2028.

4.13.3 Preparation of *[G-3] axial substituted silicon phthalocyanine* (46)

The product was synthesised and purified as described for di((3',5'-dibenzyloxy)benzyloxy)phthalocyaninato silicon , and the band at $R_f = 0.6$ collected. Pure *di-((3',5'-di(3'',5''-di(3''',5'''benzyloxy)benzyloxy)benzyloxy) benzyloxy)phthalocyaninato-silicon* was isolated as a green prismatic crystals; (38 mg, 18.4 % yield); T_g = 101.6 °C; IR (KBr disc) 3432.6, 2938.6, 2852.3, 1599.8, 1514.7, 1445.8, 1328.6, 1158.4, 1059.1 cm^{-1}; Found C, 78.06 %; H, 5.55 %; N, 2.93 %; $C_{242}H_{198}O_{30}N_8Si$ requires C, 78.00 %; H, 5.36 %; N, 3.00 %; UV/vis (solid, λ_{max} (nm)) 686, 654, 618, 359, (toluene, λ_{max} (nm)) 680, 650, 612, 332; δ_H (500 MHz, $CDCl_3$, 60 °C) -0.68 (4H, s), 3.50 (4H, d), 3.97 (8H, s), 4.85-5.10 (48H, brm), 5.61 (2H, t), 6.32 (8H, d), 6.45 (4H, t), 6.54 (8H, t), 6.65 (16H, d),7.05-7.30 (80H, m), 8.20-8.31 (8H, bm), 9.52-9.62 (8H, m); MS (FAB) found *m/e* 3726, (M^+) requires 3726.

4.14 Chapter Four References

1. Perrin, D. D., Armarego, W. L. F., *'Purification of Laboratory Chemicals,'* Pergamon Press, Oxford, 3rd. Edition, 1988

2. Kametani, T., Kano,S., *J. Pharmac. Soc. Japan*, 1962, 82, 1059

3. Reimann, E., *Chem. Ber.*, 1969, 102, 2887

4. Hawker, C. J., Fréchet, J. M. J., *J. Am. Chem. Soc.*, 1990, 112, 7638

5. Hawker, C. J., Fréchet, J. M. J., *J. Am. Chem. Soc.*, 1992, 114, 8405

6. Vowinkel, E., *Chem. Ber.*, 1996, (99), 62

7. Wooley, K. L., Hawker, C. J., Fréchet, J. M. J., *J. Am. Chem. Soc.* 1991, 113, 4252-4261

8. Kovshev, E. I., Puchnova, V. A., Luk'yanets, E. A., *Zhur. Org. Khimii.*, 1971, 7, 369

9. Kohn, M., *J. Am. Chem. Soc.*, 1951, (73), 480, *Mol. Cryst. Liq. Cryst.*, 1990 187, 365

10. Hanack, M., *Synthesis*, 1980, 287

11. Piechocki, C., Simon, J., *Nouveau Journal De Chemie*, Vol. 9, 1985, No. 3, 159

12. Kudrevich, S. V., Ali, H., van Lier, J. E., *J. Chem. Soc. Perkin Trans. 1*, 1994, 19, 2767-2774

13. Leznoff, C. C., Mougang, H., McArthur, C. R., Qin, Y., *Can. J. Chem.* 1994, Vol 72

5

Conclusions and Further Work

5.1 Conclusions and Further Work

5.1.1 Conclusions

Viable synthetic routes have been established for the preparation of axially and peripherally substituted Pc-centred dendrimers, and series of increasing dendrimer size have been synthesised in good yield.

Peripheral attachment produces dendrimers in which, perhaps surprisingly (as it may be expected that aggregation would decrease with increasing bulkiness of dendritic substituent), the Pc cores self-associate strongly in solution via cofacial interactions. These are an interesting example of cylindrical dendrimers. The strong cofacial interactions are particularly evident in the solid phase, this has subsequently been proved at Manchester by the ability of the Pcs to form spin-coated films.

The induction of glassy solid phases is an important materials property which enables thin films to be thermally processed. The lack of crystallographic domain boundaries results in non-scattering materials which are of interest for optical studies. These are currently in progress within the Physics Department, University of Manchester and by X-ray diffraction at the Synchrotron Radiation Source at the Daresbury Laboratory. Of particular interest are the robust anisotropic glasses formed by cooling the columnar mesophases of the unsymmetrical Pcs which bear only a single dendritic fragment.

Axial substitution provides Pc materials which form isotropic glasses in which cofacial association is prohibited. Edge-to-edge interactions are also minimised by the use of the larger dendritic wedges, due to the apparent tendency for the axial substituents to wrap around the edge of the Pc core. This is seen in the single crystal XRD study of Pc **(45)**, and implied by the deshielded positions of the third generation dendritic protons in the 500 MHz NMR spectrum of Pc **(46)**. Inspection of the UV/vis absorption spectra both in the solid phase and in solution also shows a red shift which decreases as the size of the dendritic substituent increases, suggesting that the Pcs become less aggregated due to a reduction in edge-to-edge interactions of the Pc cores.

5.1.2 Further Work

Fréchet's step-wise, convergent approach to the synthesis of dendrimers, although extremely time consuming, gives excellent control over the final structure of the dendrimer. Therefore, the work described in this thesis could be extended to other macrocyclic cores (e.g. naphthalocyanines, see section 4.6.7 for preliminary work). In addition the benzylic terminal groups could be replaced with other functionalities such as alkyl or water-solublising side-chains, redox active groups etc. Some of these concepts are being further pursued within the phthalocyanine group at Manchester University.

Since this work originally began, a number of different and more condensed synthetic routes to dendrimer synthesis have been described, which may be more appropriate for the preparation of dendritic wedges

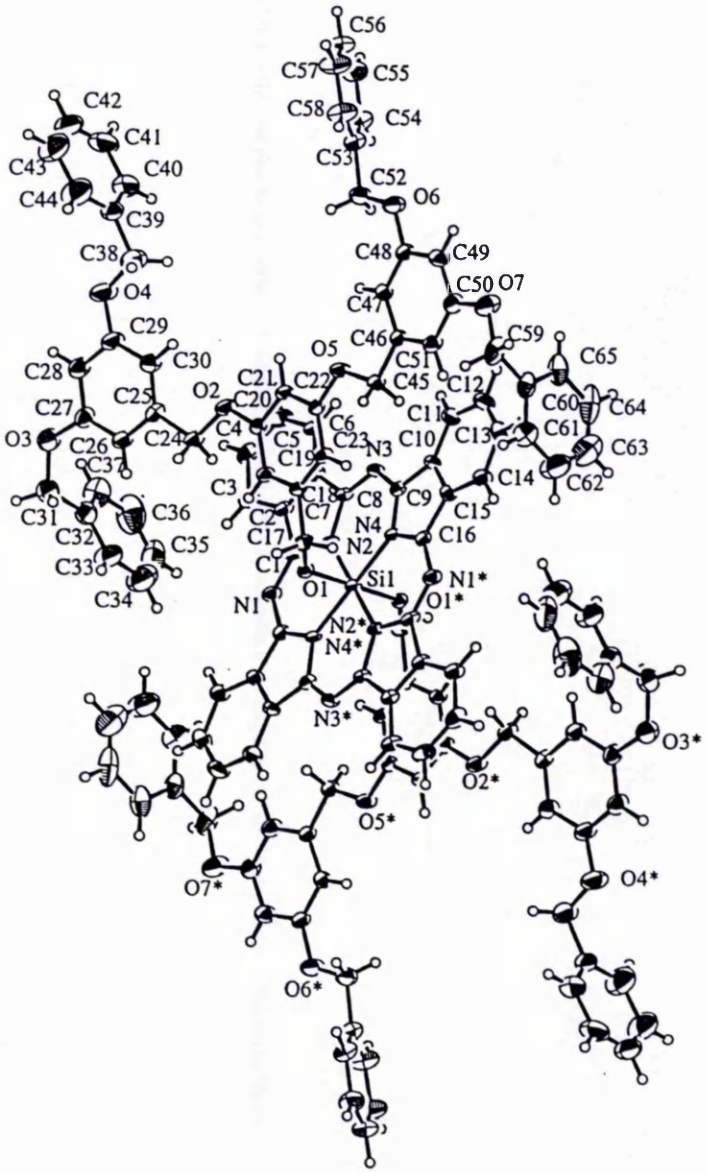
in larger quantities, and higher generations, over shorter time scales, (the most time consuming part of the work described in this thesis involved the preparation of the already published dendritic wedges !). It may be that many of the materials properties can be accomplished by using readily prepared hyperbranched polymers, as the ultimate application of dendrimers may be as useful models for the rational design of such hyperbranched polymers.

The initial interesting, and in some cases surprising results on dendritically substituted Pcs described in this thesis suggest that further work on these and similar macrocycles, would at least be of fundamental interest.

Appendix 1

X-ray Structure Report of Phthalocyanine (45)
by M. Helliwell, University of Manchester, 1996

The asymmetric unit consists of half a molecule. The Si atom lies on a centre of symmetry, and the other half of the molecule is generated by inversion.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C53
C52
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C41
C43
C40
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C48
C49
C50
O7
C47
C29
C46
C59
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C30
O5
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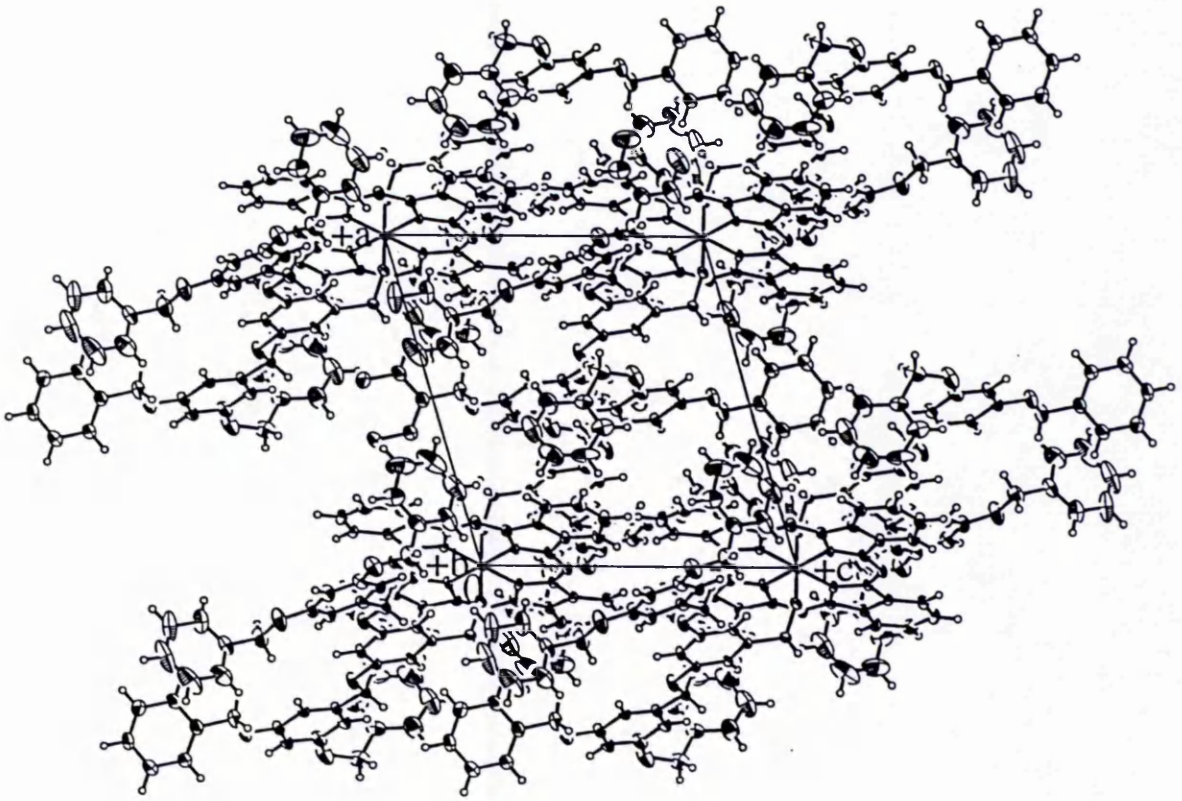
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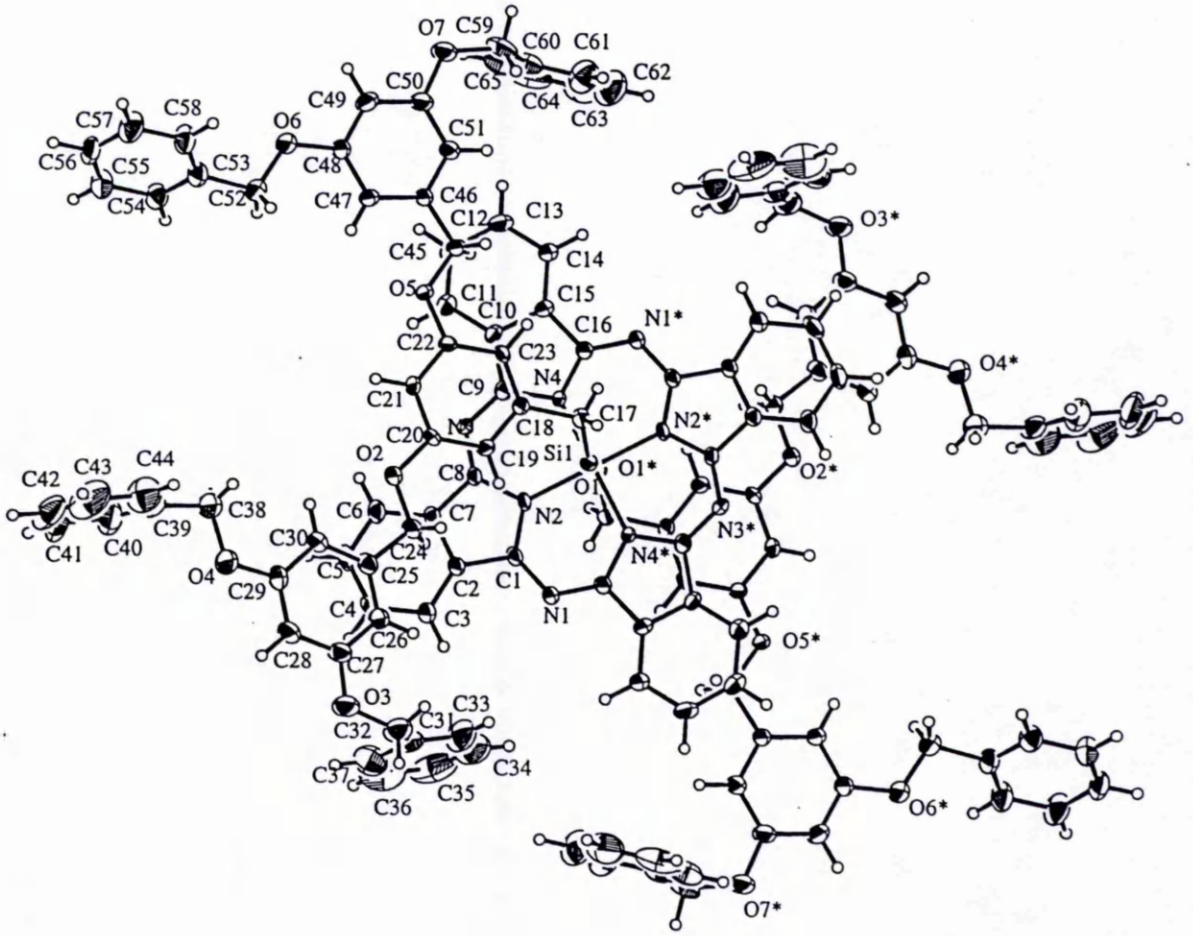
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C54
C52
C48
C47
C51
C46
C12
C13
C45
C14
O5
C11
C15
C10
C16
N1*
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C23
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C21
C9
N4
C17
O4*
N3
C18
C20
C19
Si1
O1*
N2*
O2
C8
O1
O2*
C42
C43
C44
C38
C6
C7
N2
C39
C41
C40
C30
C24
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C25
C2
C1
N4*
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C4
C3
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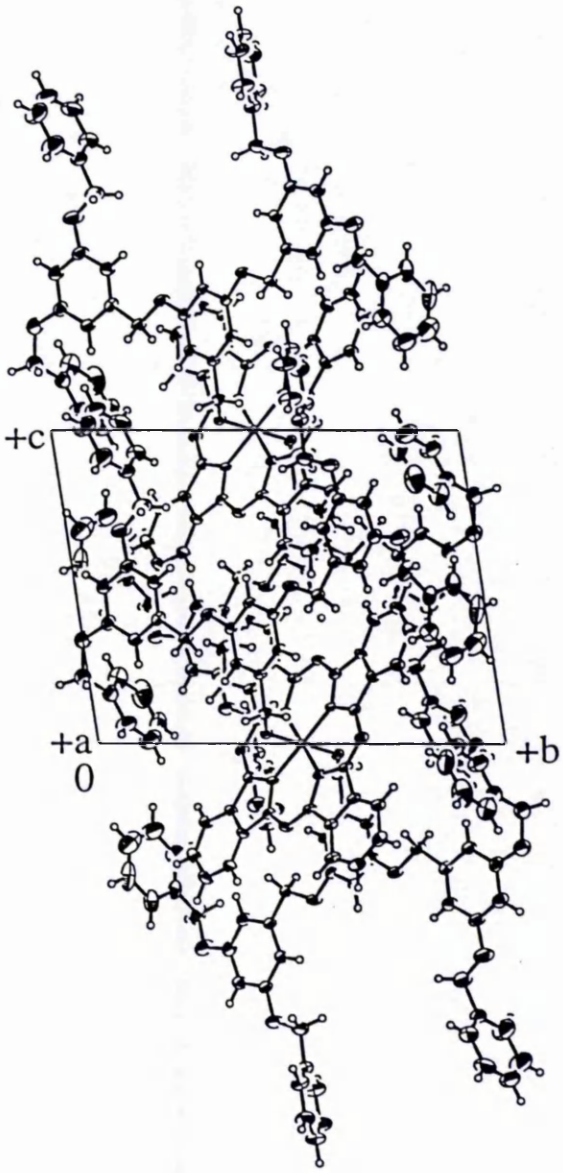
O7*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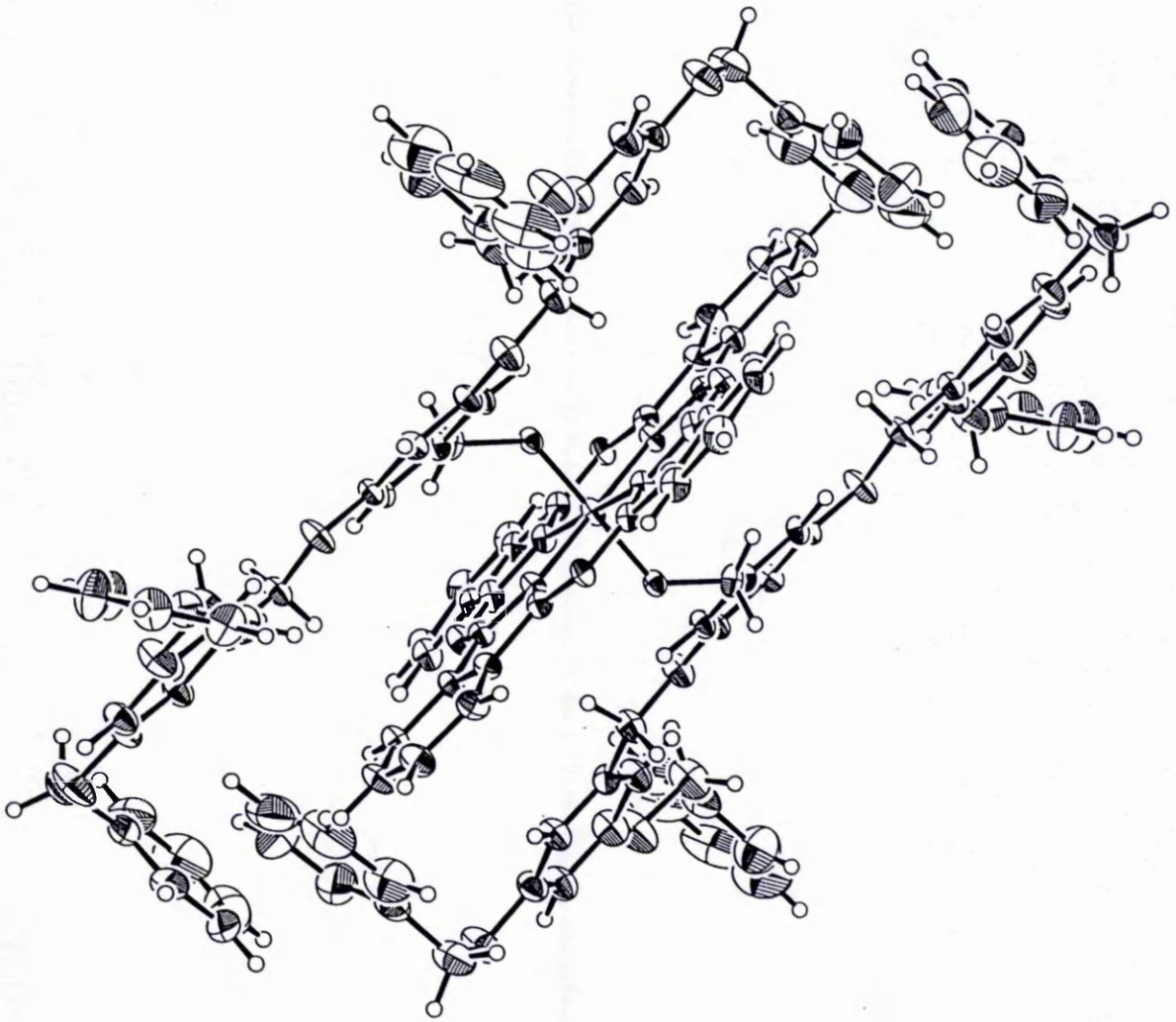

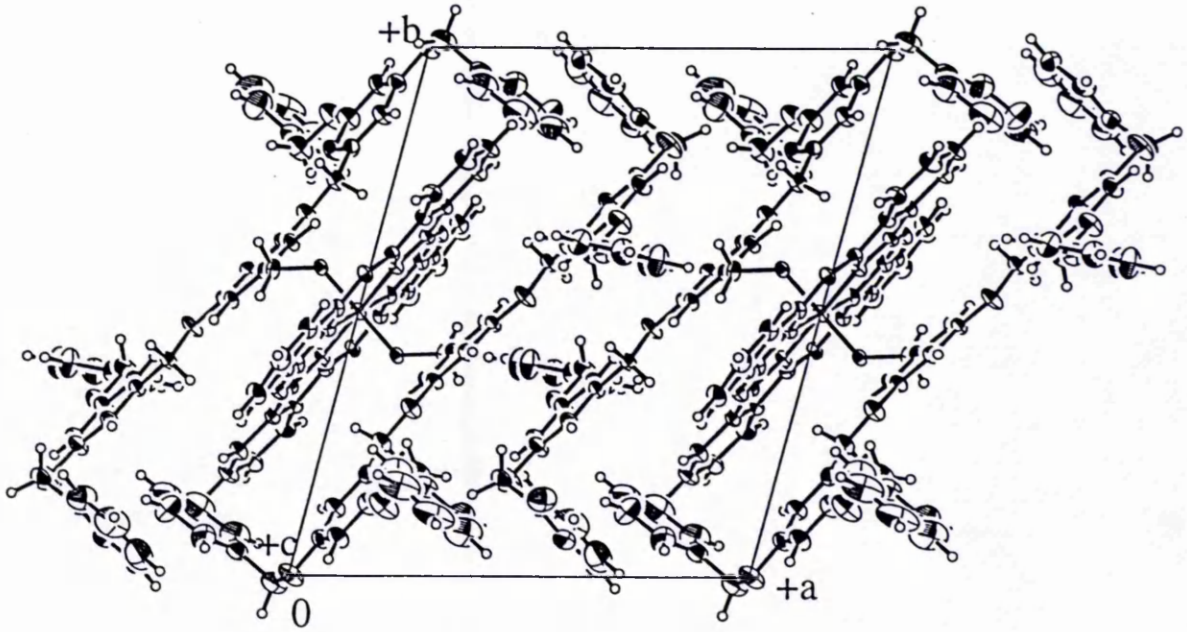
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Data Collection

An opaque prismatic crystal of $C_{130}H_{102}N_8O_{14}Si$ having approximate dimensions of 0.07 x 0.30 x 0.40 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC5R diffractometer with graphite monochromated Mo-Kα radiation and a rotating anode generator.

Cell constants and an orientation matrix for data collection , obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $16.17 < 2\theta < 23.34°$ corresponded to a primitive triclinic cell with dimensions:

a = 14.079(3) $\AA$	α = 103.62(2)°
b = 16.291(5) $\AA$	β = 109.30(2)°
c = 12.710(3) $\AA$	γ = 71.83(2)
V = 2585(1) $\AA^3$	

For Z = 1 and F.W. = 2028.37, the calculated density is 1.30 g/cm^3. Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be:

$P\bar{1}$ (#2)

The data were collected at a temperature of 20 $\pm$ 1°C using the ω-2θ scan technique to a maximum 2θ value of 50.1°. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.41° with a take-off angle of 6.0°. Scans of $(1.15 + 0.30 \tan\theta)°$ were made at a speed of 8.0°/min (in omega). The weak reflections ($I < 10.0\sigma(I)$) were rescanned (maximum of 3 scans) and the counts were accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 1.0 mm, the crystal to detector distance was 285 mm, and the detector aperture was 6.0 x 6.0 mm (horizontal x vertical).

Data Reduction

Of the 9709 reflections which were collected, 9175 were unique (R_{int} = 0.102). The intensities of three representative reflection were measured after every 150 reflections. Over the course of data collection, the standards decreased by 4.5%. A linear correction factor was applied to the data to account for this phenomenon.

The linear absorption coefficient, μ, for Mo-Kα radiation is 0.9 cm^{-1}. An empirical absorption correction based on azimuthal scans of several reflections was applied which resulted in transmission factors ranging from 0.93 to 1.00. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{130}H_{102}N_8O_{14}Si$
Formula Weight	2028.37
Crystal Color, Habit	opaque, prismatic
Crystal Dimensions	0.07 X 0.30 X 0.40 mm
Crystal System	triclinic
Lattice Type	Primitive
No. of Reflections Used for Unit Cell Determination (2θ range)	25 (16.2 - 23.3°)
Omega Scan Peak Width at Half-height	0.41°
Lattice Parameters	a = 14.079(3)Å b = 16.291(5) Å c = 12.710(3) Å α = 103.62(2)° β = 109.30(2)° γ = 71.83(2)° V = 2585(1) Å^3
Space Group	$P\bar{1}$ (#2)
Z value	1
D_{calc}	1.303 g/cm^3
F_{000}	1064.00
μ(MoKα)	0.90 cm^{-1}

B. Intensity Measurements

Diffractometer	Rigaku AFC5R
Radiation	MoKα (λ = 0.71069 Å) graphite monochromated
Attenuator	Zr foil (factors = 1.00, 1.14, 1.29, 1.47)
Take-off Angle	6.0°
Detector Aperture	6.0 mm horizontal 6.0 mm vertical
Crystal to Detector Distance	285 mm
Voltage, Current	0kV, 0mA
Temperature	20.0°C
Scan Type	ω-2θ
Scan Rate	8.0°/min (in ω) (up to 3 scans)
Scan Width	(1.15 + 0.30 tan θ)°
$2\theta_{max}$	50.1°
No. of Reflections Measured	Total: 9709 Unique: 9175 (R_{int} = 0.102)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.9331 - 1.0000) Decay (4.48% decline)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SHELXS86)
Refinement	Full-matrix least-squares
Function Minimized	$\Sigma w(\|Fo\| - \|Fc\|)^2$
Least Squares Weights	$w = \frac{1}{\sigma^2(Fo)} = [\sigma_c^2(Fo) + \frac{p^2}{4}Fo^2]^{-1}$
p-factor	0.0090
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>2.50σ(I))	4023
No. Variables	691

Reflection/Parameter Ratio	5.82
Residuals: R; Rw	0.067 ; 0.052
Goodness of Fit Indicator	1.84
Max Shift/Error in Final Cycle	0.00
Maximum peak in Final Diff. Map	0.29 $e^-/\AA^3$
Minimum peak in Final Diff. Map	-0.24 $e^-/\AA^3$

The structure was solved by direct methods[1] and expanded using Fourier techniques[2]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement[3] was based on 4023 observed reflections ($I > 2.50\sigma(I)$) and 691 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R = \Sigma||Fo| - |Fc||/\Sigma|Fo| = 0.067$$

$$R_w = \sqrt{(\Sigma w(|Fo| - |Fc|)^2/\Sigma wFo^2)} = 0.052$$

The standard deviation of an observation of unit weight[4] was 1.84. The weighting scheme was based on counting statistics and included a factor (p = 0.009) to downweight the intense reflections. Plots of $\Sigma w(|Fo| - |Fc|)^2$ versus $|Fo|$, reflection order in data collection, sin θ/λ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.29 and -0.24 $e^-/\AA^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[5] . Anomalous dispersion effects were included in Fcalc[6]; the values for Δf' and Δf" were those of Creagh and McAuley[7]. The values for the mass attenuation coefficients are those of Creagh and Hubbel[8]. All calculations were performed using the teXsan[9] crystallographic software package of Molecular Structure Corporation.

References

(1) SHELXS86: Sheldrick, G.M. (1985). In: "Crystallographic Computing 3" (Eds G.M. Sheldrick, C. Kruger and R. Goddard) Oxford University Press, pp. 175-189.

(2) DIRDIF94: Beurskens, P.T., Admiraal, G., Beurskens, G., Bosman, W.P., de Gelder, R., Israel, R. and Smits, J.M.M. (1994). The DIRDIF-94 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

(3) Least-Squares:

Function minimized: $\Sigma w(|Fo| - |Fc|)^2$

where w = $\frac{1}{\sigma^2(Fo)} = [\sigma_c^2(Fo) + \frac{p^2}{4}Fo^2]^{-1}$

$\sigma_c(Fo)$ = e.s.d. based on counting statistics

p = p-factor

(4) Standard deviation of an observation of unit weight:

$$\sqrt{\Sigma w(|Fo| - |Fc|)^2/(No - Nv)}$$

where: No = number of observations

Nv = number of variables

(5) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

The ADC (atom designator code) specifies the position of an atom in a crystal. The 5-digit number shown in the table is a composite of three one-digit numbers and one two-digit number: TA (first digit) + TB (second digit) + TC (third digit) + SN (last two digits). TA, TB and TC are the crystal lattice translation digits along cell edges a, b and c. A translation digit of 5 indicates the origin unit cell. If TA = 4, this indicates a translation of one unit cell length along the a-axis in the negative direction. Each translation digit can range in value from 1 to 9 and thus ± 4 lattice translations from the origin (TA=5, TB=5, TC=5) can be represented.

The SN, or symmetry operator number, refers to the number of the symmetry operator used to generate the coordinates of the target atom. A list of symmetry operators relevant to this structure are given below.

For a given intermolecular contact, the first atom (origin atom) is located in the origin unit cell and its position can be generated using the identity operator (SN=1). Thus, the ADC for an origin atom is always 55501. The position of the second atom (target atom) can be generated using the ADC and the coordinates of the atom in the parameter table. For example, an ADC of 47502 refers to the target atom moved through symmetry operator two, then translated -1 cell translations along the a axis, +2 cell translations along the b axis, and 0 cell translations along the c axis.

An ADC of 1 indicates an intermolecular contact between two fragments (eg. cation and anion) that reside in the same asymmetric unit.

Symmetry Operators:

(1)	X,	Y,	Z	(2)	-X,	-Y,	-Z

Appendix 2

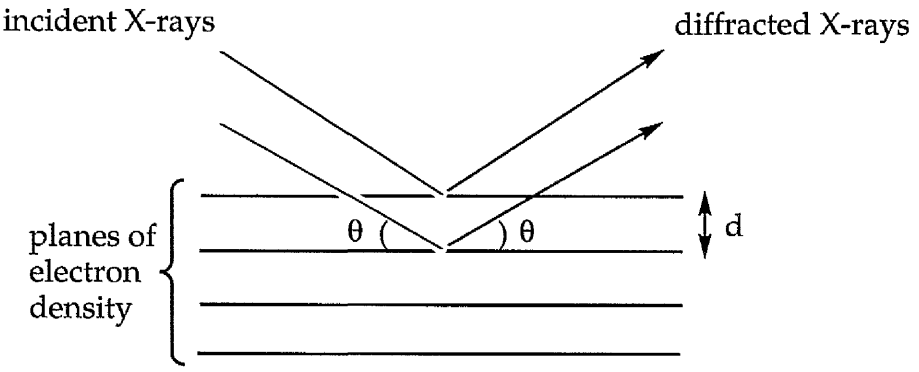
X-ray Diffraction Study of Unsymmetrical Pcs (33) - (37)

X-ray Diffraction (XRD)

X-ray diffraction is an excellent technique for determining the structure of columnar mesophases, giving diffraction patterns based on the repeat distances of the columnar lattice arrangement.[1] Much more structural information is obtained from liquid crystalline samples that are uniformly oriented. However, the highly viscous mesophases displayed by Pc derivatives make alignment into a single domain difficult and most XRD studies have been carried out on non-oriented (powder) samples. Mesophases which are structurally assigned only from microscopic textures are questionable.

Generally it is very difficult to prepare crystals of heavily substituted Pcs for single XRD studies. For example, octa-alkyl derivatives of interest due to their liquid crystal properties, usually form fibrous solid crystals that are inappropriate for single crystal studies. The diffraction patterns for some of these materials have been indexed to an orthorhombic structure containing a tilted arrangement of molecules with respect to each other.

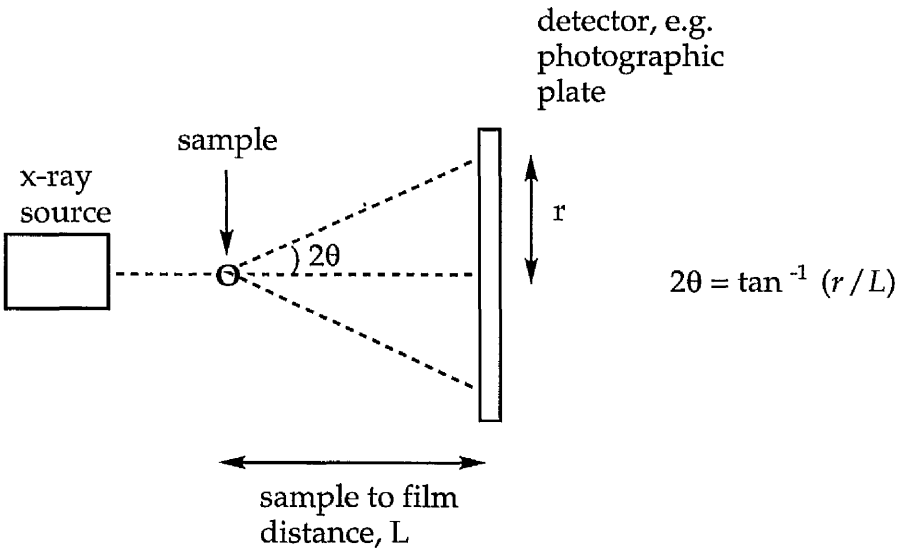
The structure of phthalocyanine mesophases can be identified by X-ray diffraction.[2] X-rays are diffracted from planes of electron density when Bragg's Law (i) is satisfied;



$$n\lambda = 2d \sin \theta \quad \text{(i)}$$

where n = order of diffraction, λ = wavelength of incident rays (Å), d = distance between planes of electron density (Å). θ = angle between planes of electron density and incident X-rays (degrees).

Therefore, if a sample of material in the liquid crystalline state is placed in a beam of X-rays, it will scatter the X-rays at a series of angles 2θ compared to the incident beam and these diffractions can be recorded photographically. Since liquid crystal samples will normally consist of a large number of domains, all with independent orientations, the resultant diffraction pattern will be a series of rings, known as a powder diffraction pattern. It is possible by using magnetic or electric fields to align the samples and consequently, gain more structural information. The d-spacings can be obtained by calculation of θ from the diffraction pattern (and the geometry of the diffraction equipment) and then by use of the Bragg equation (i).



X-ray diffraction experiment.

X-ray diffraction patterns of discotic liquid crystal phases will yield information according to the region of study.[3] In the wide angle region, $\theta > 5°$, there can be two types of diffraction occurring. The first is because of the order within the columns and can be seen either as a relatively sharp ring corresponding to the inter-disc distance (usually around 3.5 Å) in an ordered phase e.g. D_{ho} or as a broad halo centred around the same distance, but corresponding to the liquid like order within the column of a disordered phase e.g. D_{hd}. The second is due to the liquid-like order of the side-chains and occurs normally at 4 - 4.5 Å as a broad halo. The halo due to the inter-disc distance in the disordered phase is sometimes absent, possibly due to temperature effects.

At small angles of $\theta < 5°$ scattering is due to the symmetry of the columnar lattice. Here it is convenient to use parameters derived from crystallography. Any three-dimensional crystal can be described with a unit cell of molecules which is repeated a large number of times to build

the crystal. This unit cell has dimensions described by three distances a, b and c (as well as angles, but these are commonly 90° and will, therefore, be ignored here). The diffraction from a crystal will correspond to planes of electron density in the molecules. If the lattice is reconstructed in reciprocal space by plotting a^* (= $1/a$), b^* (= $1/b$), c^* (= $1/c$), then these planes can be represented by points on the lattice . Each point will have a position on each of the axes and is characterised by the number of reciprocal unit cells away from the origin in each direction. This co-ordinate corresponds to the Miller Index and for each direction a, b, and c the index is called h, k and l. The Miller Indices are expressed in the form hkl (e.g. 110, 200 etc.) The d spacing between each plane of electrons for one type of diffraction is, therefore, dependent on the Milller Indices and the reciprocal unit cell dimensions in the following manner:

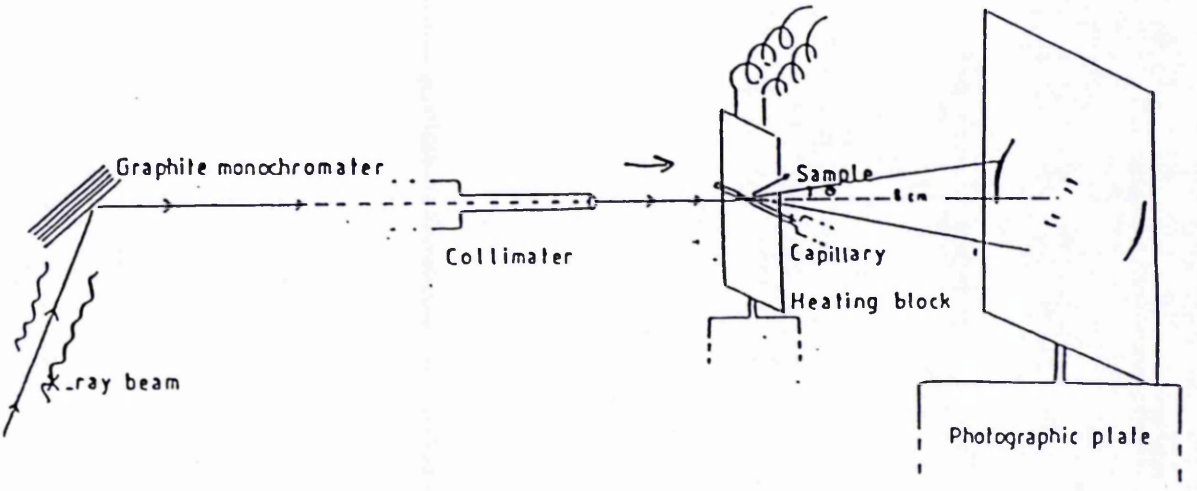
$$d = \sqrt{\frac{1}{h^2 a^{*2} + k^2 b^{*2} + l^2 c^{*2}}}$$

The solving of this crystallographic equation is highly complex and is usually now computer aided. However, if a two dimensional lattice only is considered, the situation is simplified greatly. The lattice parameters l and c can be disregarded as the d-spacing is now solely dependent on a, h, b and k. For discotic liquid crystals, the two-dimensional lattice gives well distinguished diffraction patterns, because a hexagonal lattice requires, for a peak to be seen, that the expression $h + k = 2n$ (n is an integer) is satisfied. Therefore, reflections which are distinguished include 110, 200, 020, 220, 310, 130, 400, 040 etc. Also because $a = \sqrt{3}b$ for hexagonal symmetry, the set of reflections for each of 110 and 200, 310 and 020, 400 and 220, 130 and 420 are coincident. The powder diffraction of such a system will, therefore, give a set of sharp rings with the innermost

corresponding to the 110 / 200 reflection being the most intense. If these rings are present, they can be, without doubt, assigned to a two-dimensional hexagonal lattice.

X-ray Diffraction Study

Powder X-ray diffraction studies were recorded at varying temperatures for Pc's **(33)-(37)**. The X-ray source used was Cu/K_α radiation of wavelength λ = 1.54 Å and the measurements made at 40 KV, 20 MA. The sample to film distance was 6.0 cm.



Schematic diagram for the X-ray instrument.

If a hexagonal mesophase were present the low angle X-ray would show two distinct rings corresponding to spacing (referred to as d_1 and d_2) in the ratio of 1: $\sqrt{3}$, characteristic of a two dimensional lattice.

Calculation of intercolumnar distance (d_1)

$\tan 2\theta$ = radius (r)/D where D = sample to film distance (eq. 1)

From Bragg's law $\lambda = 2\, d \sin\theta$

Thus, $\delta = \lambda/2\, d \sin\theta$ (eq. 2)

For hexagonal lattice $d_1 = \sqrt{3}.\, d_2$ and $a = \sqrt{3}.\, b$

$a^* = 1/a$

$b^* = 1/b$

also,

$\sin\theta / \lambda = 1/2\, \sqrt{h^2 a^{*2} + k^2 b^{*2}}$ where h and k are Miller indices

Combining equations 2 and 3,

$d = 1/\sqrt{(h^2 a^{*2} + k^2 b^{*2})}$ $b = a/\sqrt{3} \Rightarrow b^* = \sqrt{3}.\, a^*$

and $d = 1/\sqrt{(h^2 a^{*2} + k^2 3a^{*2})}$ which rearranges to;

$d = 1/(h^2 + 3k^{*2})^{1/2} . (a^{*2})^{1/2}$ $= 1/(h^2 + 3k^2)^{1/2} . a^*$

Thus, $\mathbf{d = a/(h^2 + 3k^2)^{1/2}}$ (h, k = 1, 1 and 2, 0)

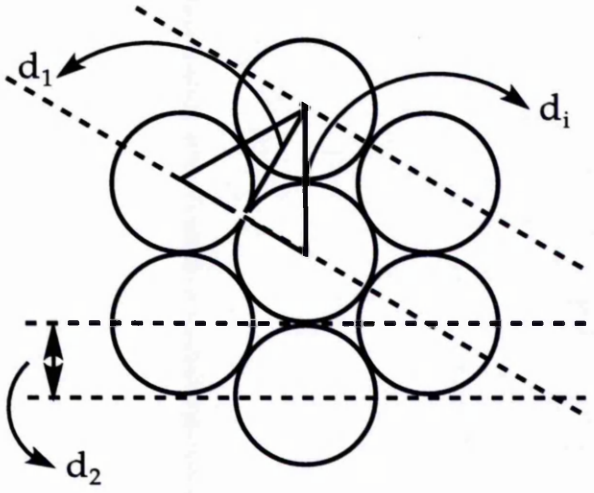
The (100) reflection d_1 can be taken from the graphs in appendix 2. This is calculated from the diameter of the inner ring, which we call x, this corresponds (eq. 2) to r = 1/2 x

From equation 1 (r = 1/2 x, D = 6.0cm), therefore θ can be calculated.

From equation 2, $d_1 = 1.54/2 \sin\theta$, therefore d_1 can be calculated.

Similarly from the diameter of the outer ring ($r = 1/2\, x_2$) therefore θ can be calculated and d_2 can be calculated from equation 2.

Pcs **(33)-(37)** were investigated at different temperatures. The intercolumnar distances (d_i) can be calculated by simple geometry;



Assignment of the first two inner rings observed for a hexagonal lattice.

Therefore;

Cos 30 = d_1/d_i, For Pc **(33)** at 25 °C d_1 = 23.8 Å

d_i = 23.8/cos 30

Intercolumnar distance (d_i) = 27.48 Å

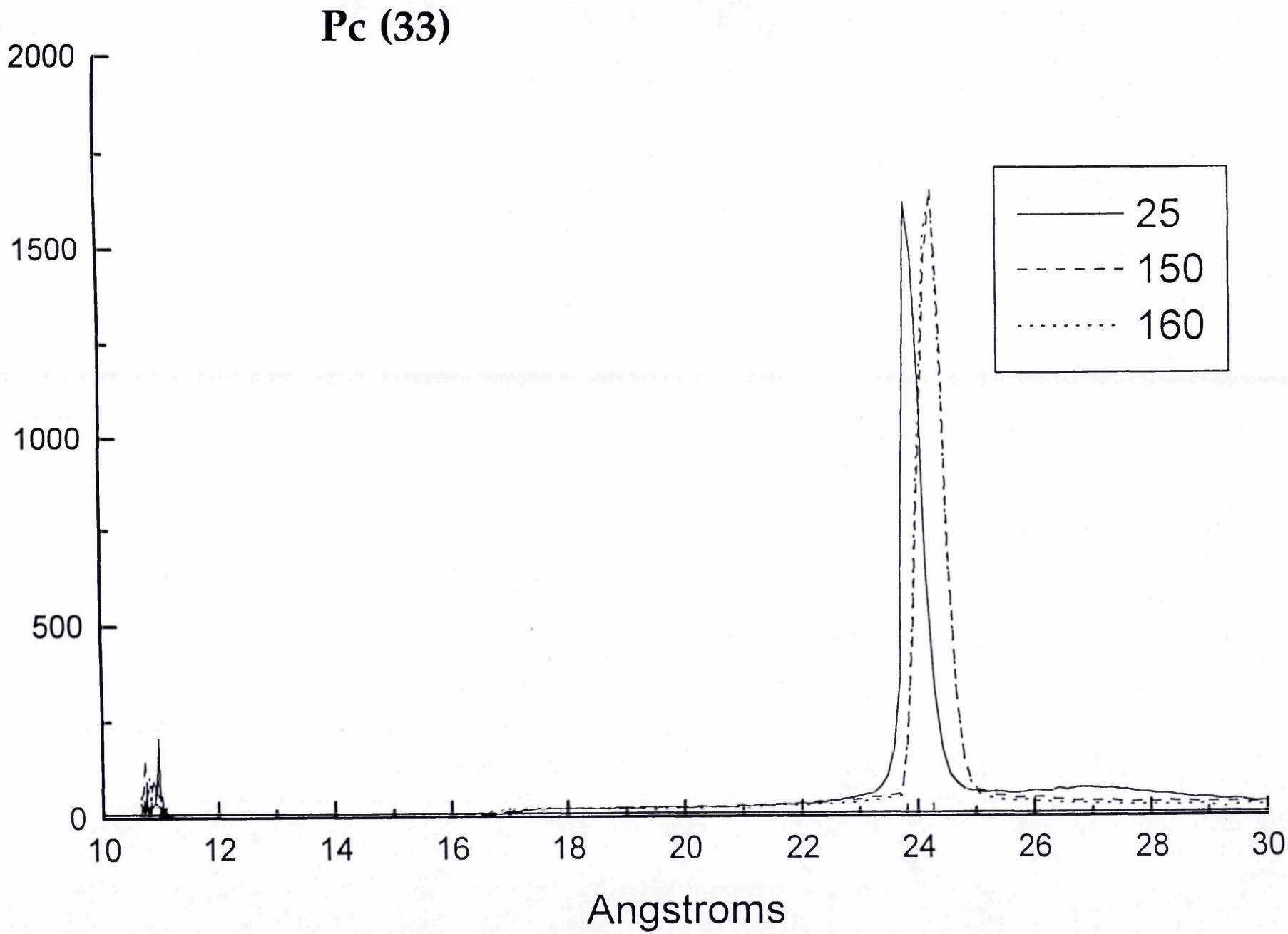
Similarly at 150 °C d_1 = 24.3 Å, therefore **d_i = 24.3/ cos 30 = 28.06 Å**

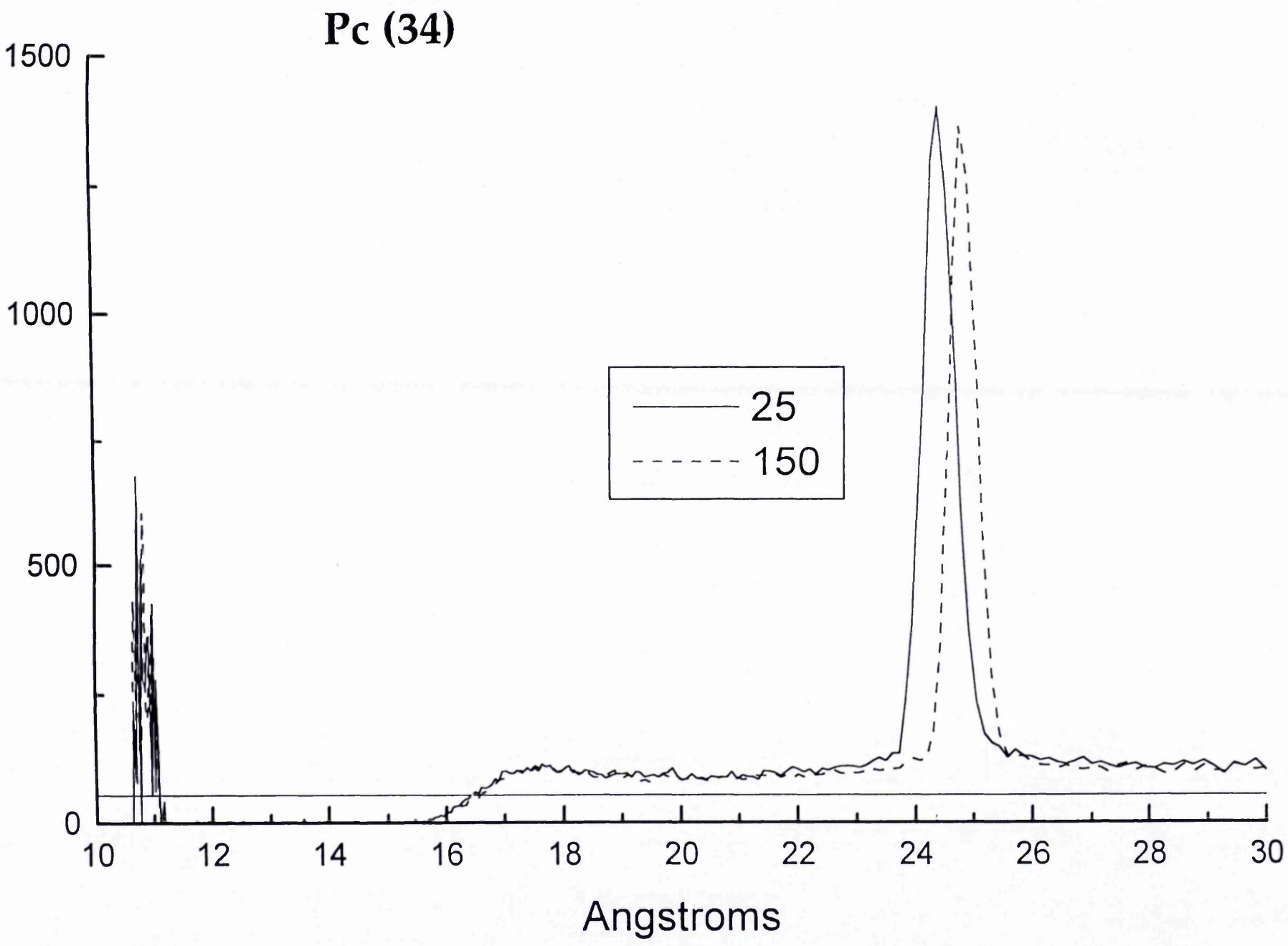
From the data obtained (see graphs at the end of chapter), it can be concluded that for the series of mixed phthalocyanines investigated, there is no d_2 ring observed. Therefore, there is no direct evidence of a hexagonal structure from the X-ray data. The lack of (110) diffraction however, indicates disorder as would be expected from these unsymmetrical molecules.

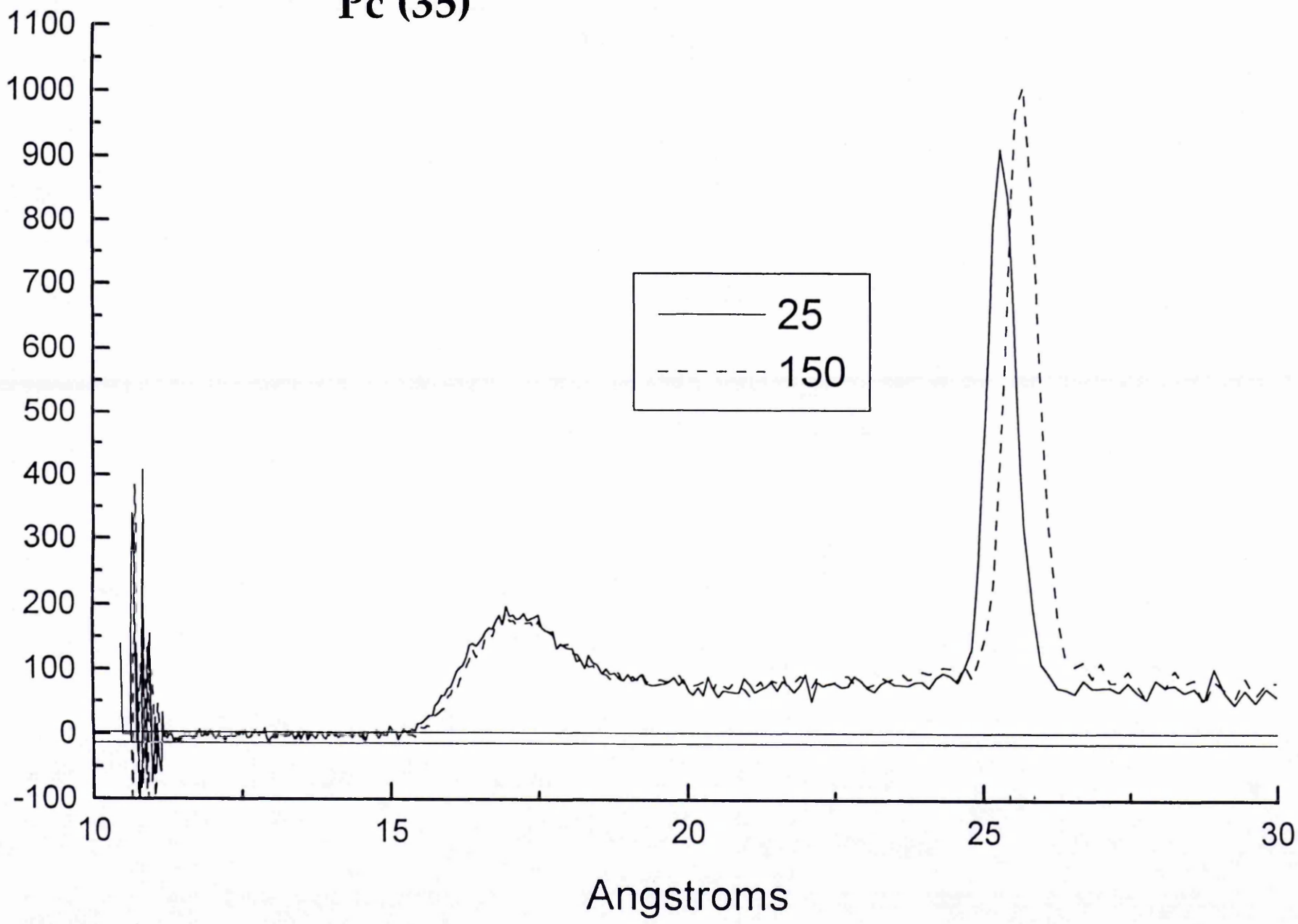
Pc	Temp °C	d_1 Å	d_i Å
Mono [G-1] **(33)**	25	23.8	27.48
Mono [G-1] **(33)**	150	24.3	28.06
Di [G-1] **(34)**	25	24.4	28.18
Di [G-1] **(34)**	150	25	28.87
Mono [G-2] **(35)**	25	25.5	29.45
Mono [G-2] **(35)**	150	26	30.02
Di [G-2] **(36)**	150	29.1	33.60
Mono [G-3] **(37)**	25	29.9	34.53

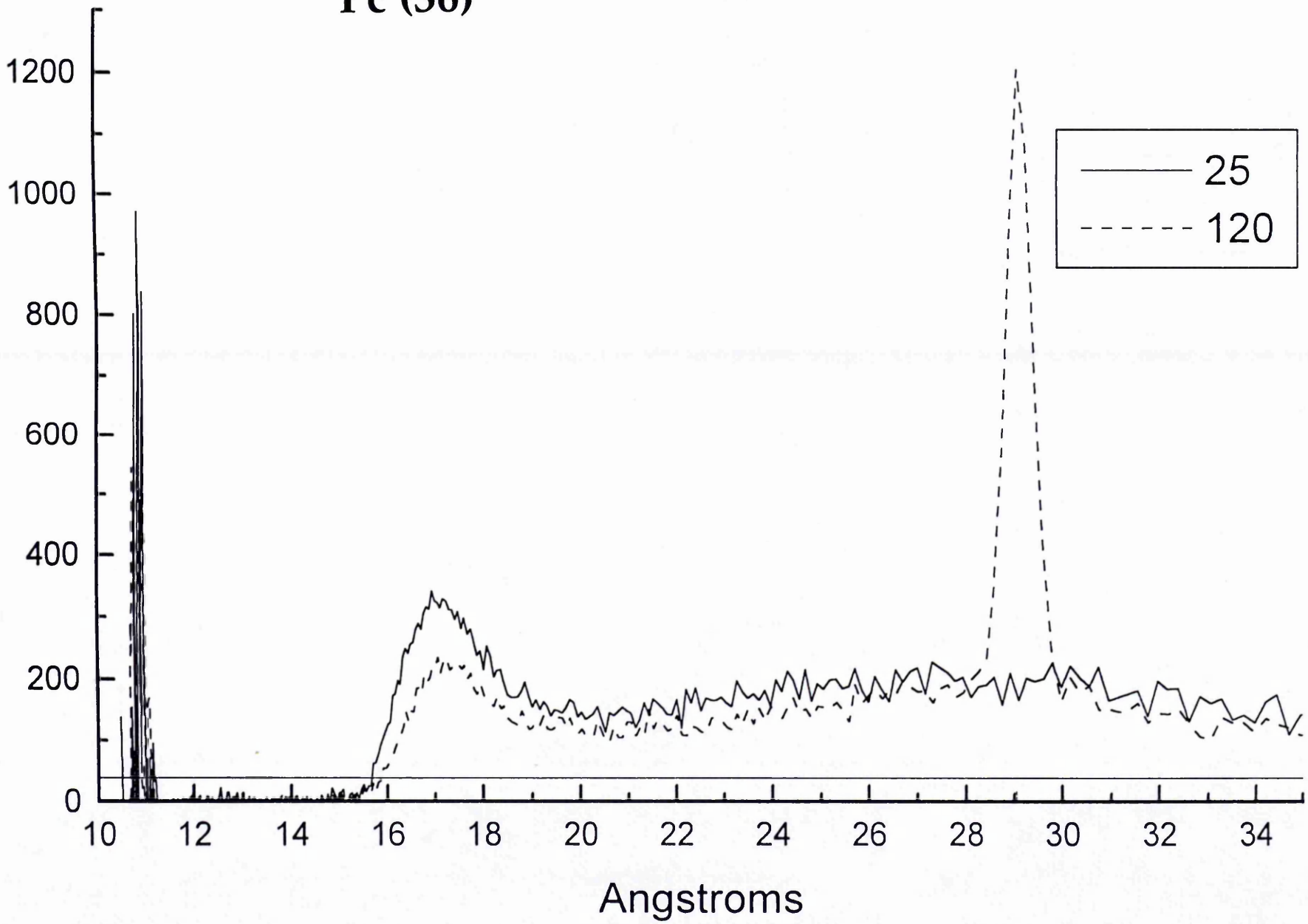
Table of intercolumnar distances (d_i) obtained from X-ray diffraction data.

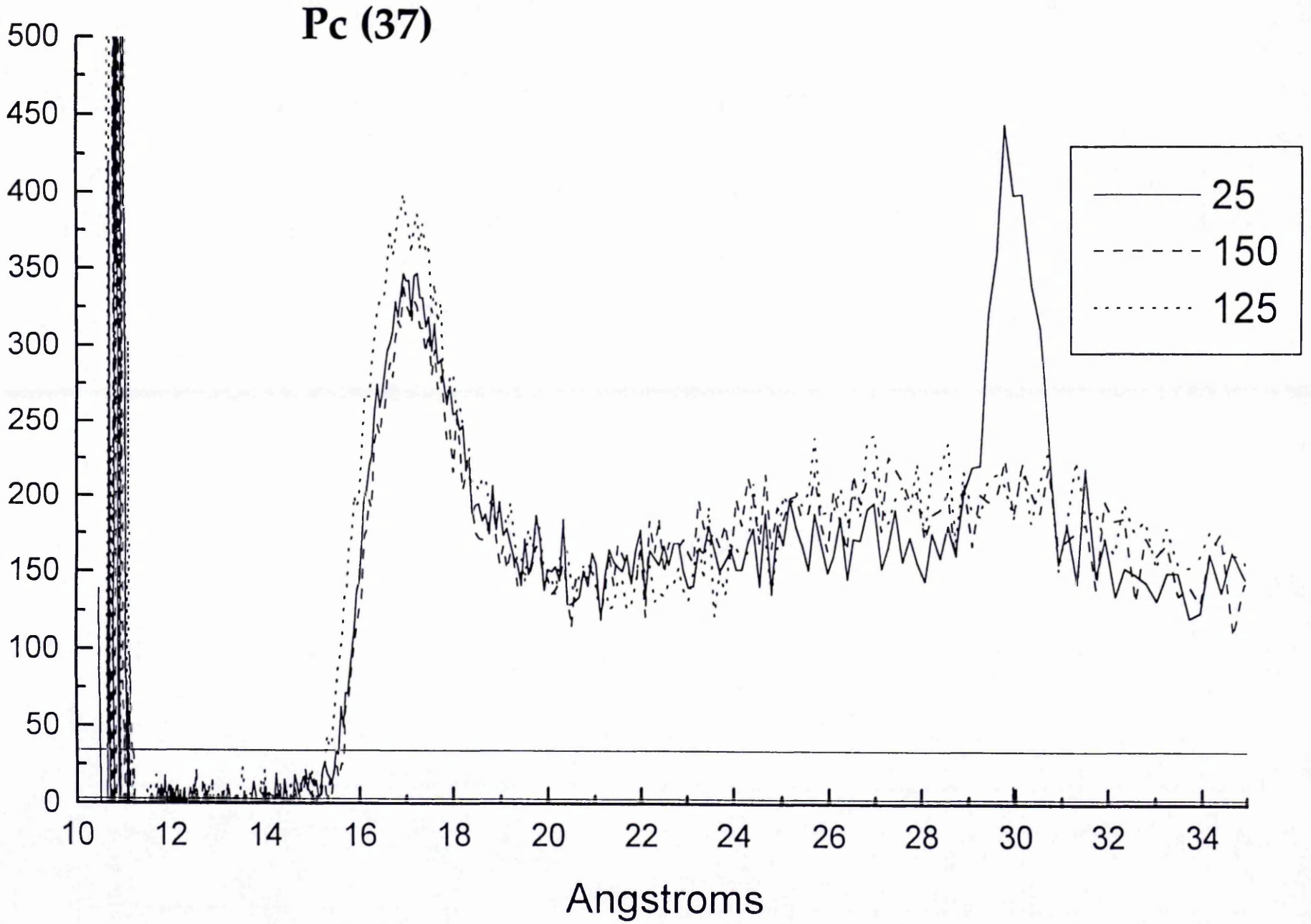
The other phases also have a characteristic diffraction pattern of rings, allowing them to be identified. This is because each two-dimensional lattice has its own rule of extinction (peaks which are not present). Once the parameters *a* and *b* are calculated the values of *h* and *k* can be found for each peak and fitted to a known extinction rule. Certain reflections, particularly if the temperature of the phase is too high, or there are no coincident peaks are too weak to be observed. Therefore, it may not be possible to distinguish between mesophases, because not enough characteristic diffractions are available. In the case of lamellar phases, the only factor which contributes to the low angle diffraction is the parameter *c*. This gives rise to a diffraction pattern with the d-spacings in the ratio of 1 : 1/2 : 1/3 : 1/4. It is sometimes the case that X-ray diffraction is not conclusive in identifying the phase as the data cannot be indexed to any known lattice.


Pc (33)
2000
1500
1000
500
0
10
12
14
16
18
20
22
24
26
28
30
Angstroms
25
150
160


Pc (34)
1500
1000
500
0
25
150
10
12
14
16
18
20
22
24
26
28
30
Angstroms


Pc (35)
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
10
15
20
25
30
Angstroms
25
150


Pc (36)
1200
1000
800
600
400
200
0
10
12
14
16
18
20
22
24
26
28
30
32
34
Angstroms
25
120


Pc (37)
500
450
400
350
300
250
200
150
100
50
0
10
12
14
16
18
20
22
24
26
28
30
32
34
Angstroms
25
150
125

Appendix 2 References

1. Cherodian, A. S., Davies, A. N., Richardson, R. M., Cook, M. J., McKeown, N. B., Thomson, A. J., Feinjoo, J., Ungar, G., Harrison, K. J., *Molecular Crystals and Liquid Crystals*, 1991, 196, 103-14

2. Stout, G. H., Jenson, L. H., *'X-ray Structure and Determination - A Practical guide'* Macmillan, 1968

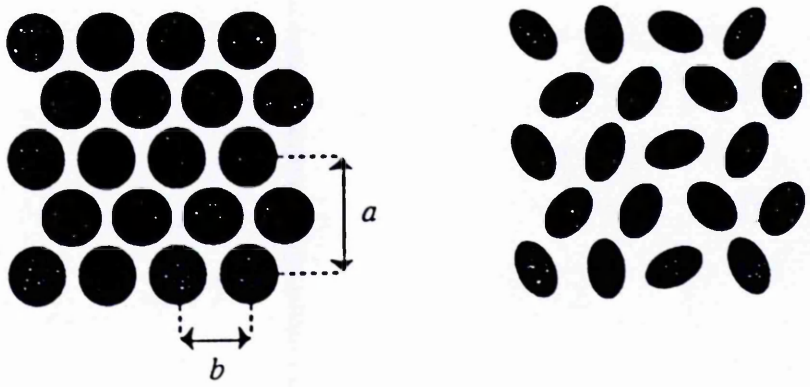
3. Simon, J., Bassoul, P., *'Phthalocyanines - Properties and Applications,'* Eds. C. C. Leznoff and A. B. P. Lever, VCH, Vol 2, 1989, 223-299

Appendix 3

Determination of Columnar Mesophase

Columnar Mesophases

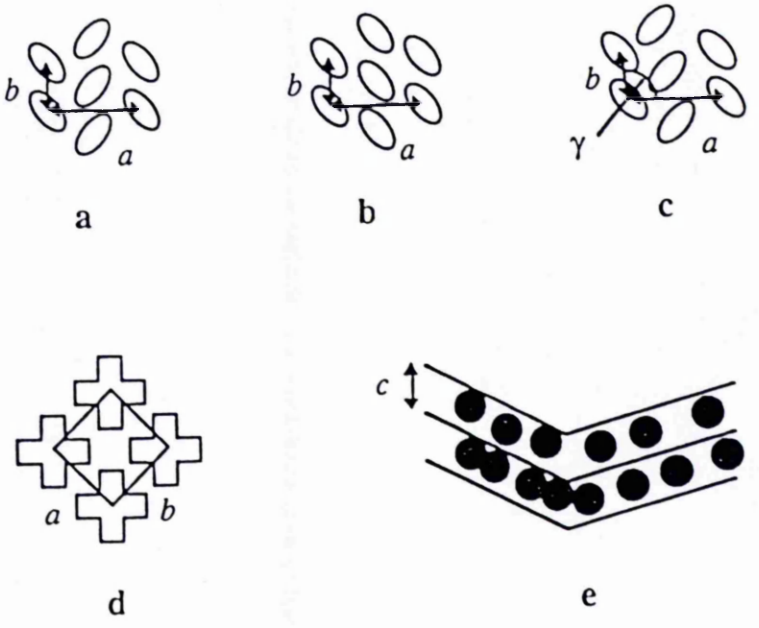
Columnar mesophases are categorised according to the degree of order within and the packing of the columns.[1] The columns are commonly arranged in a two dimensional hexagonal array as this is the simplest way of packing discs. Although the Pc molecules themselves are strictly not disc shaped, since they are spinning within the columns, their average shape will approximate to a disc. The molecules within the columns may be orthogonal or tilted with respect to the axis of the column. If the crystallographic parameters are taken as a and b, then for a hexagonal lattice $a = \sqrt{3}b$.



Hexagonal Lattices for Columnar Phases. Discs can be perpendicular to the axis of the column, or tilted with no correlation of tilts between the columns.

Other commonly encountered lattices for the columns include rectangular (D_{rd}), tilted (D_t), oblique ($D_{ob.d}$), tetragonal (D_{tet}) and lamellar (D_L). For the D_{rd}, D_t and $D_{ob.d}$ phases the molecules do not meet the crystallographic requirement of $\sqrt{3}b$ for a hexagonal lattice, as they are

tilted within their columns. The D_t phase has a face-centred array, whilst the D_{rd} phase is non-centred and is sub-divided into different groups according to the columnar arrangement. The phases can be described by their crystallographic space groups, which refer to the lattice symmetry, the most common of these space groups being $P2_1/$. Similar symmetry is seen in the oblique arrangement, but the lattice parameters are no longer perpendicular and an angle γ is needed to describe the tilt of the molecules.



Other lattice symmetries for Discotic Mesophases. (a) $D_{rd(P2_1/a)}$ (b) D_t (c) $D_{ob.d}$ (d) D_{tet} (e) D_L. Ellipses in a, b and c represent columns of tilted molecules, crosses in black circles represent molecules.

The tetragonal arrangement in the D_{tet} mesophase is a result of the limitation of rotational movement of the molecules within the columns. In Pcs, therefore, this leads to a close packing in a tetragonal manner as the

lattice parameters *a* and *b* are equal and the Pc molecules symmetrical. The discotic lamellar mesophase D_L is not composed of columns, but of layers of molecules.[2, 3] However, the lamellar order only extends in one dimension, whilst liquid like order exists within the layers. This can be compared with the disordered stacking of molecules within disordered columnar mesophases.

As well as being characterised due to the packing of columns in two dimensions, columnar mesophases can be characterised in the third dimension, according to order within the columns. In the first case there is only short-range liquid like order of the molecules within the columns and in the second, the molecules are distributed regularly along the columns, leading to long range order within the columns, but no correlation of order between them. This is described by using the letter d (disordered) or o (ordered) after the letter used to describe the columnar lattice. Thus the two states D_{hd} and D_{ho} describe the two different types of hexagonal phase.

Appendix 3 References

1. Destrade, C., Foucher, P., Gasparoux, H., Huu Tinh, N., Levelut, A. M., Malthete, J., *Mol. Cryst. Liq. Cryst.*, 1991, 203, 149

2. Ohta, K., Muroki, H., Tagaki, A., Hatada, K., Ema, H., Yamamoto, I., Matsuzaki, K., *Mol. Cryst. Liq. Cryst*, 1986, 140, 131

3. Yakashita, H., Nishitani, A., Sumiya, Y., Terauchi, H., Ohta, K., Yamamoto, I., *Mol. Cryst. Liq. Cryst*, 1991, 163, 211