NOVEL PHTHALOCYANINES WITH OUT – OF – PLANE SUBSTITUENTS

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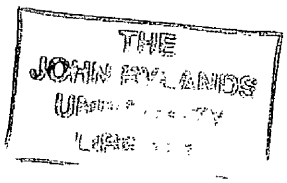

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Abstract

The aim of this project was to synthesise, and study the properties of a number of novel substituted phthalocyanine (Pc) derivatives. A series of indane based phthalonitriles with aliphatic substituents was prepared, and the behaviour of the Pc derivatives produced via a standard Pc tetra-cyclisation reaction observed. The aggregation in solution of the resultant Pcs were then be studied utilising UV spectroscopy, and in the solid state via microscopy. The materials were found to exhibit discotic liquid crystalline behaviour.

Following this work, methodology was developed to use the core indane structure as a base for Pcs designed with the capacity for further functionalisation. The introduction of ethyl ester moieties on the indane ring allowed the synthesis of several functionalised Pcs, including the synthesis of an unsymmetrical phthalocyanine containing a barbituric acid moiety. This led to the investigation into the employment of Pcs in supra-molecular chemistry, and the attempted construction of a Pc 'ladder' pseudo polymer.

The synthesis of ketal-type analogues of the indane system was attempted, but cyclisation of the 'ketal' monomeric phthalonitrile to form the tetramer proved unsuccessful.

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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Acknowledgements

The author would like to take the opportunity to thank all those who made the completion of this thesis possible. Most importantly, thanks are due to Dr. Neil McKeown for his guidance and support over several years. EPSRC and Avecia are also due thanks for their financial support. The technical staff within the Chemistry Department merit more than a small mention for their tolerance of my endless questioning and use of their machines, especially Val and John. Andy L, for both the scientific and alcoholic input; Genome, Hall et al for the latter; Smithers and the rest of the lab for making life even more interesting, N, S and F for putting up with me, and finally all and sundry who joined me on my perambulation through the last few years.

Preface

The Author of this thesis graduated in 1999 from the University of Manchester with a 2:1 MChem Honours Degree in Chemistry. The degree included a one year industrial placement with SmithKline Beecham, developing novel pharmaceutical products.

The research represented in this thesis was carried out as part of a PhD course at the University of Manchester from 1999 to 2002.

Abbreviations

AcOH	Acetic acid	NMR	Nuclear Magnetic Resonance
BA	Barbituric acid	NEt_3	Triethylamine
DCM	Dichloromethane	Pc	Phthalocyanine
DMF	Dimethylformamide	PeOH	Pentanol
DMSO	Dimethylsulfoxide	PHMS	Poly(methylhydrosiloxane)
Et	Ethyl	NBS	N-Bromosuccinimide
IR	Infra-red	S	Smectic
LC	Liquid Crystal	tBu	Tertiary Butyl
MALDI	Matrix Assisted Laser Desorption Ionisation	THF	Tetrahydrofuran
		pTsOH	(para)Toluene sulfonic acid
MeOH	Methanol	UV	Ultra-violet
N	Nematic	XRD	X-ray diffraction
TAP	Triaminopyrimidine		

1.0: Introduction to Phthalocyanines

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Phthalocyanine[1] (usually abbreviated to Pc) is a nitrogen containing macrocycle, an analogue of the naturally occurring porphryin ring system. The latter is well known in combination with iron in haemoglobin, the oxygen binding protein in red blood cells.

There are several unusual aspects of the Pc structure (and its derivatives) that make the material worthy of investigation. The physical behaviour of the substance has led to a variety of uses, and there are many more potential applications in development.

1.1: A Brief history of Phthalocyanine:

The material phthalocyanine was first developed in the early years of the 20th century in the search (as with other compounds developed at this time) for stable non-aqueous-soluble dyestuffs.

Pc was initially observed as a strongly coloured by-product in the synthesis of ortho- (1,2) disubstituted phenyl compounds[2]. The investigation into the precise structure of this unusual macrocycle was first conducted by the chemist Reginald P. Linstead[3], in conjunction with ICI.

Linstead demonstrated that Pc is a symmetrical macrocycle formed from four iminoisoindolene units. This structure generates a central cavity, capable of chelating a variety of different cations, thus altering the behaviour of the organic ring (c.f. porphryin). Linstead derived the term "phthalocyanine" from a combination of the Greek naptha (rock oil) and cyanine (blue). With respect to the material's similarity to the porphryin ring, the

alternative nomenclature for Pc is tetrabenzotetraazoporphryin (with reference to the four benzenoid subunits and the nitrogen atoms at the four meso positions) as in Figure 1.

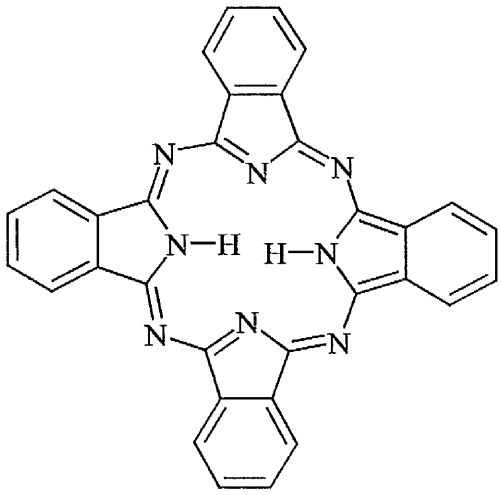


Figure 1: Phthalocyanine

1.2: Uses of Phthalocyanines:

The original development of Pcs as dyestuffs proved to be very successful, and Pcs are still used currently for this purpose[4]. However, a variety of other applications have been developed and are in development. These include molecular electronics[5,6], non-linear optics[7,8,9], photodynamic therapy[10,11], liquid crystals[12,13], catalysis[4,14], and fields as diverse as xerography[15,16] and solar energy conversion[17].

As the scale of electronic components reduces almost exponentially, it has been suggested that molecule sized electronics could be possible, and development of Pcs for this purpose has been speculated[5,6]. Another electrical effect is the photoelectric behaviour of the material: useful in the technology of xerography[15,16] – Pcs are used as photoconducting pigments in photocopiers and laser printers – a constantly expanding area of research. The effect of sunlight on the substance indicates use as a converter of solar energy[17], and this is in development. Pcs have possibilities as potential liquid crystal displays[12,13]. In the LC

state, the disk-like molecules can form partially ordered columns much like conventional "rod-like" LCs. Nematic phases (with partial order) and smectic (ordered) phases have been observed, leading to fabrication as LCDs.

In the area of catalysis[4,14], the capability to reduce oxygen has led to use in electrical energy production, as well as the formation of hydrogen from water for use as fuel has been demonstrated. Removal of thiols from crude oil can be achieved using Pcs, as can more common household deodorising mixtures (via removal of hydrogen sulfide). Further uses of Pcs utilising zeolite cages will appear soon.

The dramatic effect of atmospheric gases on the material (for example the reaction with oxygen) has led to the fabrication of pollution sensors monitoring nitrogen dioxide, chlorine and carbon monoxide concentrations. Also possible is humidity monitoring. The catalytic properties of Pcs have also led to biosensors, monitoring cholesterol, cysteine and glutathione from blood plasma. An application showing great potential is the field of photodynamic therapy[10,11]: Pcs tend to be preferentially taken up by certain target body tissues (e.g. tumour cells). Irradiation by red (and near IR) light appears to cause tissue decay in the area of the tumour thought to be by formation of singlet oxygen within the cancerous cells.

The overall future for phthalocyanines appears to be varied to the extreme. Further developments of the material may lead to uses in a number of different fields. Time will tell the value of this group of materials.

1.3: Optical Properties of the Molecule

The key feature of the molecule and its derivatives that aroused initial interest among chemists is the extremely strong absorption of light exhibited by phthalocyanines. This is driven by aromatic nature of the Pc core (18 e- - thus following Hückel's rule for conjugated π – systems). This results in the characteristic Q – band in the visible spectrum[18]. Coupled with the position of the Soret band[19], this gives the material its deep blue – green colour in solution. Colour is dependant on chelated metal and substituents – copper centred Pcs are generally blue; and octa-alkoxy substituted Pcs tend to be green, due to the substituents moving the Soret band to the blue region of the visible spectrum. The Q – band may be a single peak (metallated Pc) or split as a doublet (unmetallated). This effect is due to the degree of symmetry within the molecule: metallated Pcs have D4h symmetry, leading to a doubly degenerate excited state as in Figure 2, whereas unmetallated Pcs have D2h symmetry, and this reduction in symmetry results in a loss of degeneracy in the excited state and the observed pair of peaks as in Figure 3.

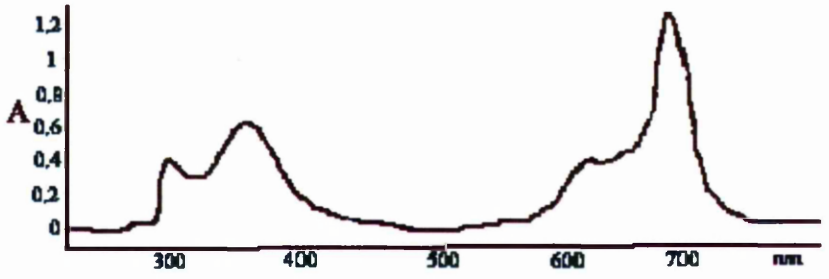


Figure 2: Uv-Vis spectrum of metallated Pc, showing Soret band at 360nm

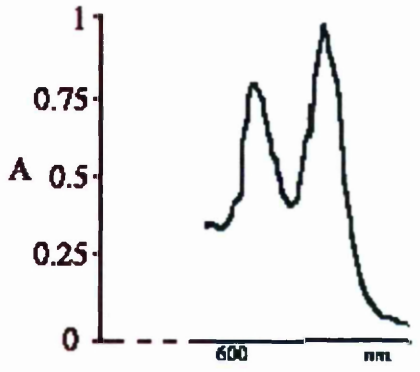
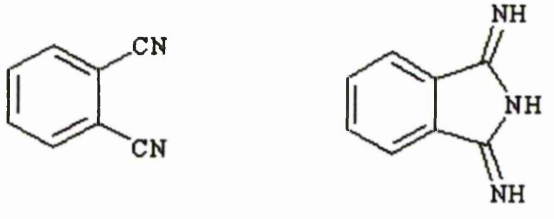


Figure 3: Q-band of unmetallated Pc

1.4: Synthesis of Pc and its Derivatives

The synthesis of Pc and its derivatives can be achieved from a variety of organic compounds. The preferred route is via *ortho* (1,2) disubstituted benzene derivatives. For the generation of non-metal chelated Pcs, the usual starting materials are either phthalonitrile or diiminoisoindoline based materials (Figure 4).



Phthalonitrile **Diiminoisoindoline**

Figure 4: Phthalonitrile and diiminoisoindoline

Direct synthesis from a phthalonitrile derivative can be achieved by reaction with lithium in refluxing pentanol (i), followed by hydrolysis. Alternatively, tetracyclisation can occur through fusing the subunits with hydroquinone (ii). Another option is to heat the phthalonitrile in DBN (1,8-diazabicyclo[4.3.0]non-5-ene) (iii)[20].

The synthesis utilising diiminoisoindoline has also proved successful. The isoindoline can be formed from phthalonitrile with ammonia refluxing in a methanol and sodium methoxide mixture (iv). Isolation of the product diiminoisoindoline could be followed by reflux in a high boiling alcohol to give the product Pc (v) (Figure 5).

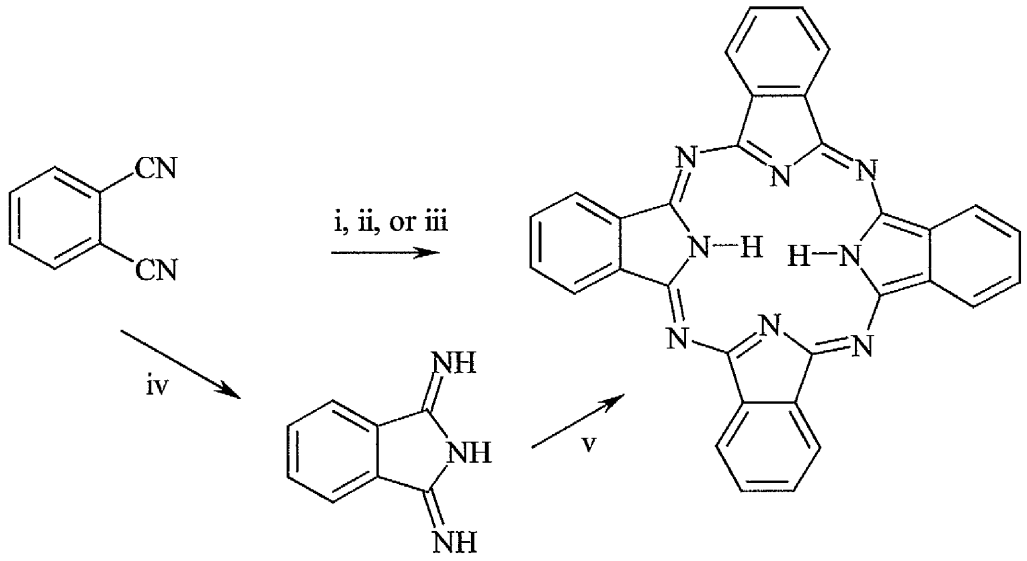
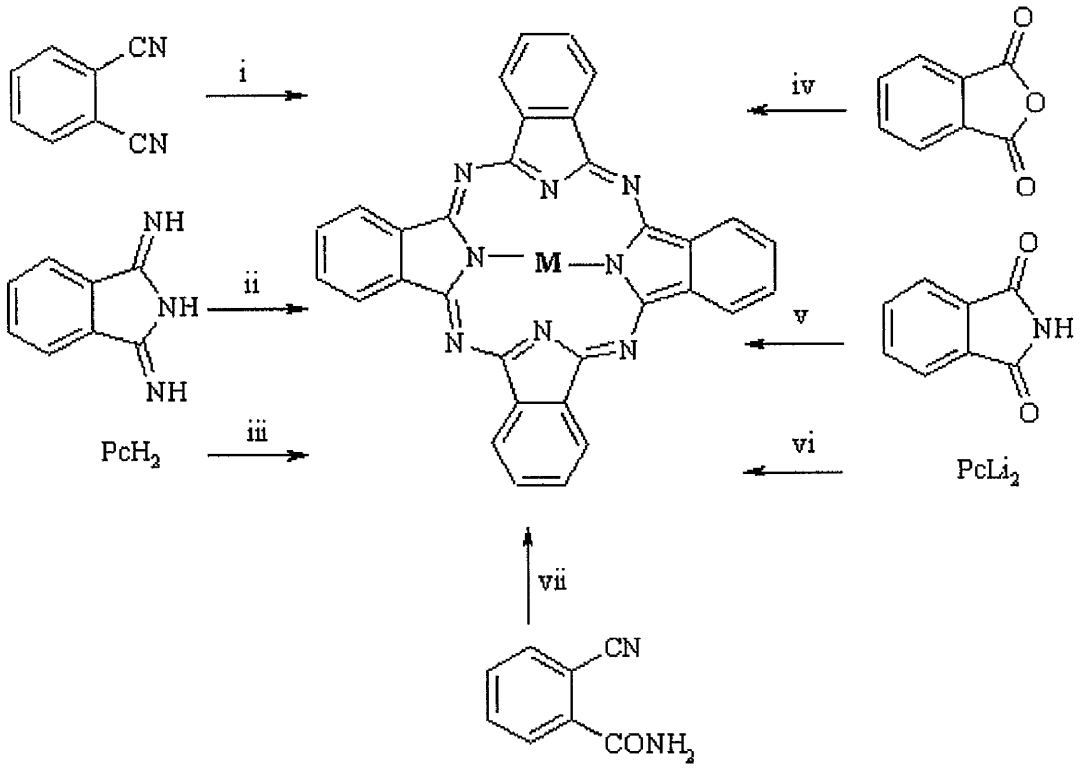


Figure 5: Formation of phthalocyanine from phthalonitrile

1.5: Metal Containing Pcs:

One of the key structural features of the material is the ability to chelate most of the elements in the Periodic Table. Metal Pcs are the most common targets for this type of synthesis. The general synthetic strategy for the production of such compounds is the use of the metal (as a salt) as a template for the tetracyclisation. This can be demonstrated using one of several starting materials: phthalimide, phthalic anhydride, the cyclised H_2Pc, Li_2Pc, phthalonitrile, diimminoisoindoline, or the 2-cyano benzamide (Figure 6).



i: M, ROH; ii: MX_2, solv.; iii: MX_2, solv. heat; iv: MX_2, urea, solv. heat;
v: MCl_2, formamide; vi: MX, solv. r.t.; vii: M, heat, dry

Figure 6: Routes to metallated phthalocyanine

The subunits are heated in a high boiling solvent with a metal salt or the metal, and (in the case of phthalic anhydride derivatives) a source of nitrogen, usually urea. Alternatively, the benzamide is cyclised in the melt.

1.6: Synthesis of substituted Pcs

Unsubstituted Pcs are generally difficult to analyse and use in the fabrication of materials, due to their low degree of solubility in most organic solvents. Solubility is greatly increased by the introduction of benzo substituents. Resultant Pcs are usually either tetra or octa substituted in the peripheral or non-peripheral positions. The introduction of substituents has two effects: the reduction of the intermolecular forces causing decreased solubility, and the possibility of novel properties in the substituted products. Increased

solubility allows standard purification techniques such as chromatography to be applied to the material, as well as a broad range of analytical techniques such as NMR (though Pcs showing high degrees of aggregation require variable temperature NMR to collect well defined spectra).

With regard to the materials properties of substituted Pcs, substituents may alter the Soret (B) band or the visible region absorption (Q) band; or induce liquid crystalline properties (especially with long alkyl chain substituents)[12], affect the packing of the material in the solid state[21], or aggregation in the solution state.

Two approaches lend themselves to the synthesis of substituted Pcs: functionalisation of the pre-formed phthalocyanine or synthesis of a substituted Pc precursor prior to cyclisation.

1.6.1: Substitution of Pre-Formed Phthalocyanines

Direct substitution of the pre-formed Pc ring is a less common method of forming substituted phthalocyanines. There are exceptions to this, specifically in the commercial synthesis of sulfonated and halogenated Pcs for dyes and pigments, and sulfonated and carboxylated Pcs used in fuel sweetening and sulfur extraction. These reactions tend to generate a mixture of products, difficult to separate and thus inappropriate for the fabrication of many devices.

Axially substituted phthalocyanines have been produced[22], with a view to increasing solubility, reduce co-facial interactions and introduce novel optical and electronic effects. There are literature examples of axially substituted TiPc, SiPc, VPc, GePc and SnPc via

covalent bonds, and also various ligands have been reported to form co-ordination bonds with central metal ions. Cyclisation of a phthalonitrile or diiminoisoindoline in the presence of the metal chloride gives the metal centred Pc with axial chlorides. Hydrolysis results in the formation of axial hydroxyl groups, which can be used to attach other moieties. Examples published include dendritic species[23].

1.6.2: Synthesis via a Substituted Precursor

i) Tetra – substituted Phthalocyanines

Four commonly studied Pcs are those prepared from t-butyl phthalonitrile, nitro-substituted phthalonitrile and its alkoxy substituted derivative and alkylated phthalic anhydride (Figure 7).

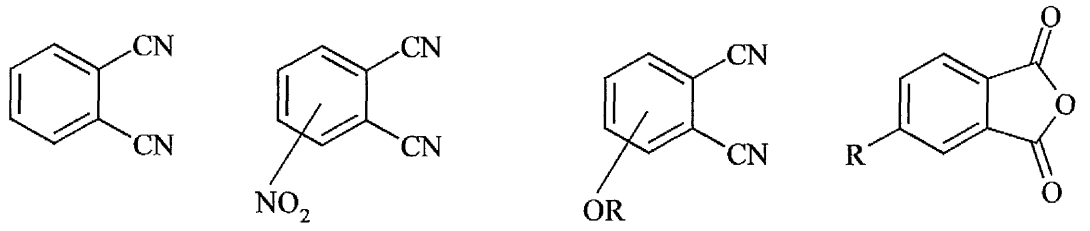
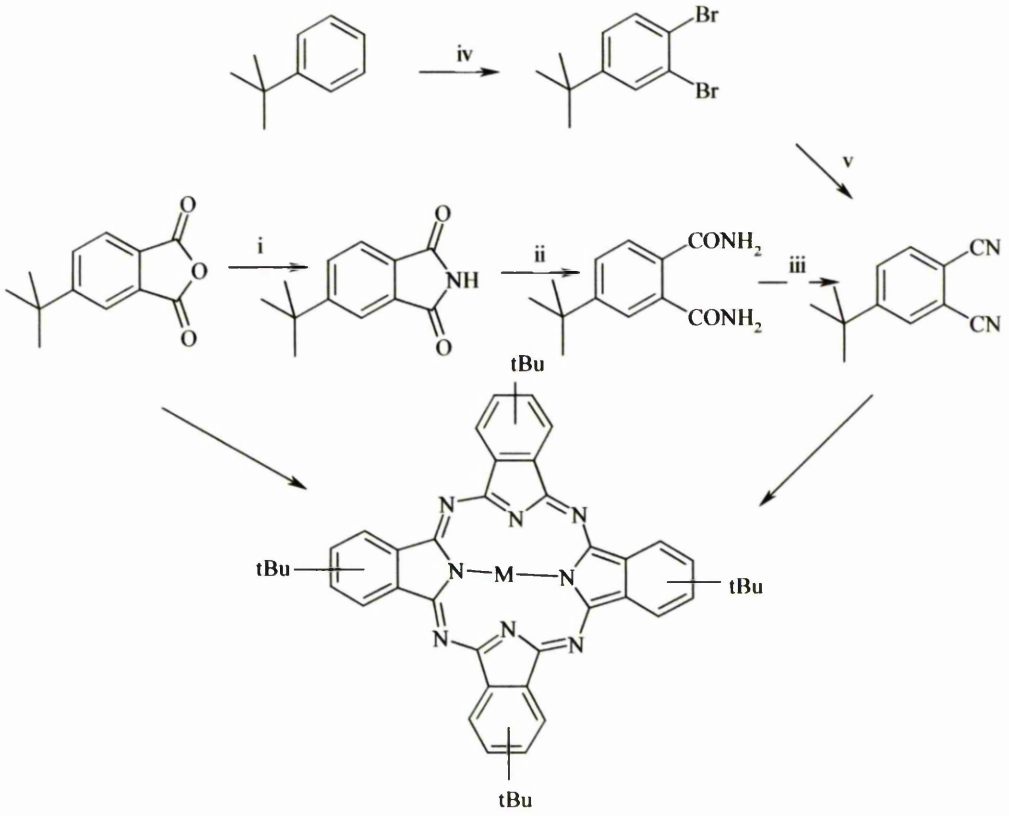


Figure 7: Substrates for the formation of tetra substituted Pcs

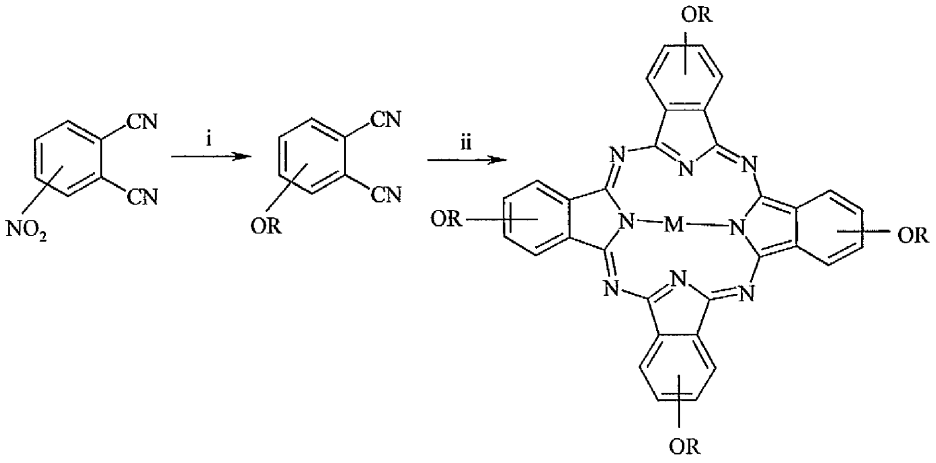
Tetra-t-butyl-MPc is of interest due to the solubilising effect of the t-butyl substituents, and their minimal effect on other physical properties of the material – thus providing a good model for the Pc system. Two synthetic routes to this compound have been described[24] (Figure 8).



i: Urea, heat; ii: NH_3; iii:PCl_5; iv: Br_2, Fe, DCM; v:CuCN, DMF

Figure 8: Routes to tetra tBu Pc

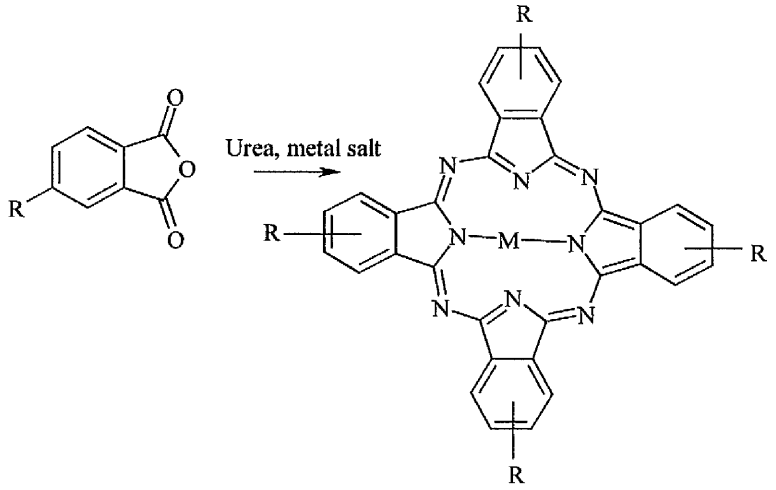
The synthesis of further functionalised tetra-substituted Pcs is commonly achieved via a nitro-substituted phthalonitrile. Aromatic nucleophilic substitution allows synthesis of the aryl ether[25,26] or thioether[27,28] derivative, followed by cyclisation to give a variety of substituted products (Figure 9).



i: Alcohol, K_2CO_3, DMF; ii: cyclisation

Figure 9: Route to tetra alkoxy Pc

An alternative route to some tetra-substituted Pcs is through the use of substituted phthalic anhydrides[29] (Figure 10). This route gives access to aqueous soluble Pcs such as tetra-sulfoxylated and carboxylated phthalocyanines. This method also gives the opportunity to introduce amide moieties to the Pc, through further functionalisation of the carboxylic acid groups.



R = tBu, CO_2H, SO_3H

Figure 10: Route to metallated tetra substituted Pc

Tetra-substituted phthalocyanines are usually formed as a mixture of regioisomers of D_{2h}, C_{4h}, C_{2v} and C_s symmetries (Figure 11).

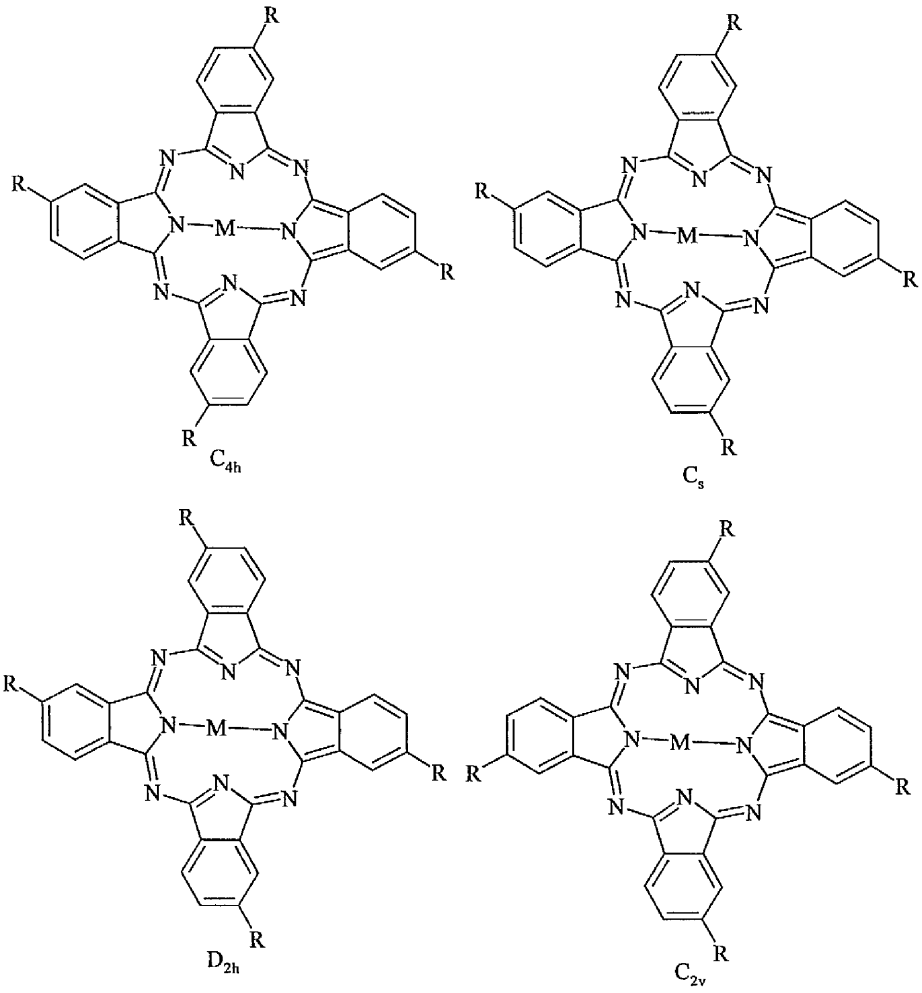


Figure 11: Regioisomers of tetra substituted Pcs

The product ratio for the formation of this mixture of products can be statistically calculated to be C_{4h}:C_s:D_{2h}:C_{2v} = 1:4:1:2. Dependant on substituents, it is possible to separate the isomers[30,31,32], for example in the case of tetra-t-butyl metallated phthalocyanine via chromatography. The existence of the four regioisomers leads to an increase in the disorder of the system in the solid state. However, if a single isomer is required, for example in the fabrication of devices for molecular electronics, then this isomeric mixture is a disadvantage.

ii) Non-peripheral Octa-substituted Phthalocyanines

The most obvious method for the preparation of the necessary 3,6-disubstituted 1,2-dicyano species would be bromination with elemental bromine followed by cyanation via the Rosenmund-von Braun reaction. However, due to steric reasons, 1,4-disubstituted aromatic species do not undergo 2,3-dibromination, tending to substitute in the 2,5 positions (Figure 12).

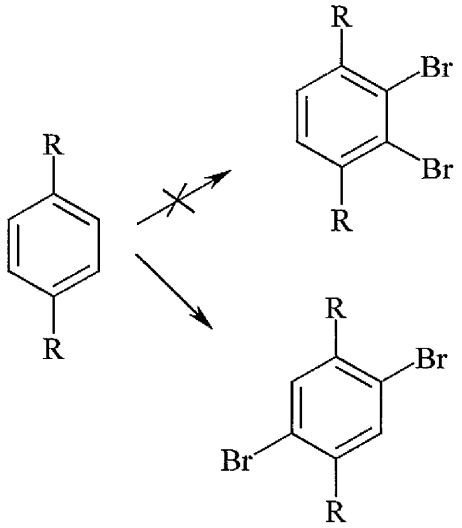
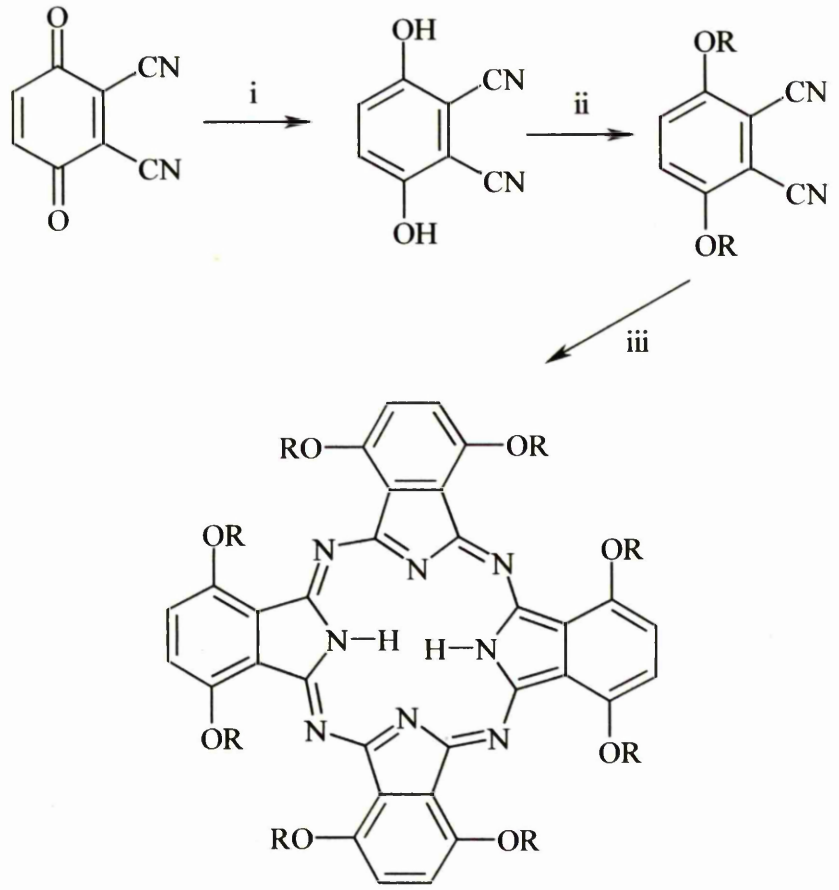


Figure 12: Bromination of 1,4-disubstituted aromatic species

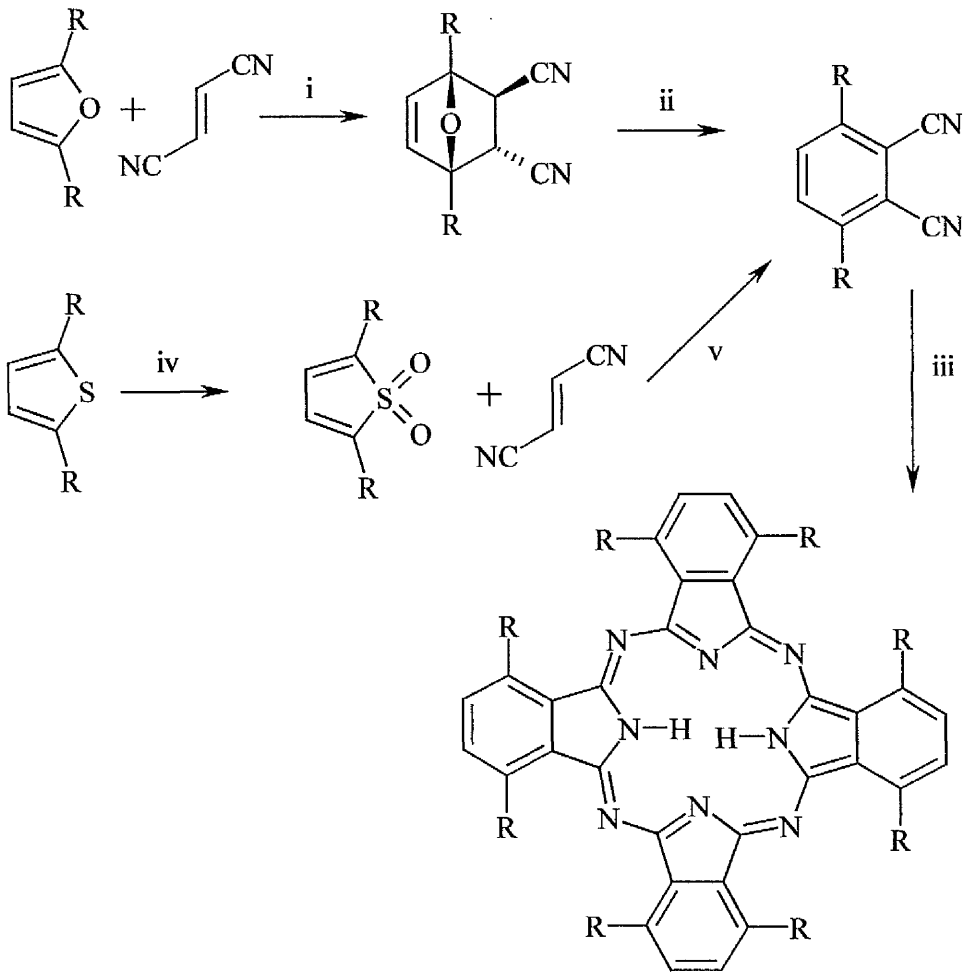
Various methods have been developed to facilitate the synthesis of 3,6-disubstituted phthalonitriles. These compounds can be readily cyclised to the resultant non-peripherally octa-substituted phthalocyanines. 3,6-Dialkoxy phthalonitriles can be synthesised in a straightforward manner from the 2,3-dicyanohydroquinone[33] (Figure 13).



i: $Na_2S_2O_5$, H_2O; ii: RX, K_2CO_3, Acetone; iii:Li, PeOH, aqueous hydrolysis

Figure 13: Synthesis of octa alkoxy non peripherally substituted Pcs

However, more 3,6-disubstituted phthalonitriles presented a more complex challenge. The two methods now employed are referred to as the furan and thiophene routes. In both routes the key step is the Diels Alder reaction of the five-membered heterocycle with fumaronitrile[34] (Figure 14).



i: Acetone, cold; ii: lithium bis(trimethylsilyl) amide, THF; iii: Li, PeOH, aqueous hydrolysis; iv: 3-chloroperbenzoic acid, DCM; v: 200 degrees

Figure 14: The furan and thiophene methods of synthesising non peripherally substituted Pcs

As a general rule, the thiophene route tends to be a more efficient method of synthesising alkylated Pcs with non-peripheral substituents, but the furan route is more versatile, giving access to protected carboxylic acids or alcohols.

iii) Peripherally octa-Substituted Phthalocyanines

The preparation of octa-peripherally substituted phthalocyanines is usually achieved via the synthesis of the equivalent 4,5-disubstituted phthalonitrile followed by cyclisation. Frequently, 1,2-disubstituted benzene derivatives are brominated, and the dibromo species converted to the desired phthalonitrile via the Rosenmund-von Braun reaction. Alkoxy substituted phthalonitriles are formed by alkylation of catechol, followed by bromination and cyanation[35]; alkylated phthalonitriles by metal catalysed alkylation of 1,2-dichlorobenzene, followed by bromination and cyanation as for 4,5-dialkoxy derivatives[36]. Synthesis of phthalonitriles with oxymethylene linkers to pendant alkyl chains can be achieved by aromatic bromination of o-xylene, followed by bromination at methyl positions and displacement of bromine from the resultant methylenes with alkoxides[37] (Figure 15).

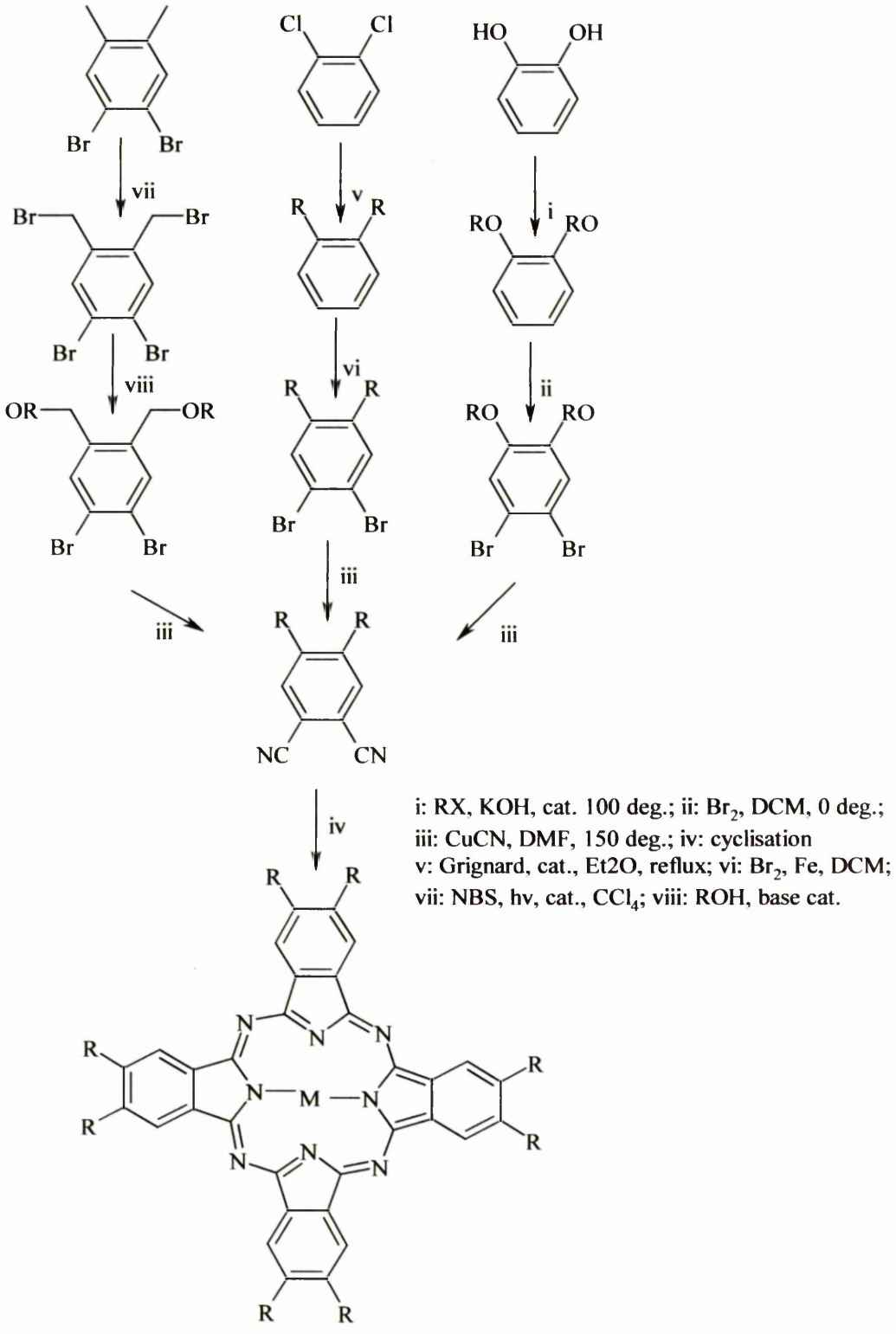


Figure 15: Routes to peripherally substituted Pcs

The synthesis of a phthalocyanine functionalised with four crown ether moieties has been achieved using similar methodology. Benzo-18-crown-6 has been brominated, cyanated and cyclised to form the cyclised product[38a] (Figure 16):

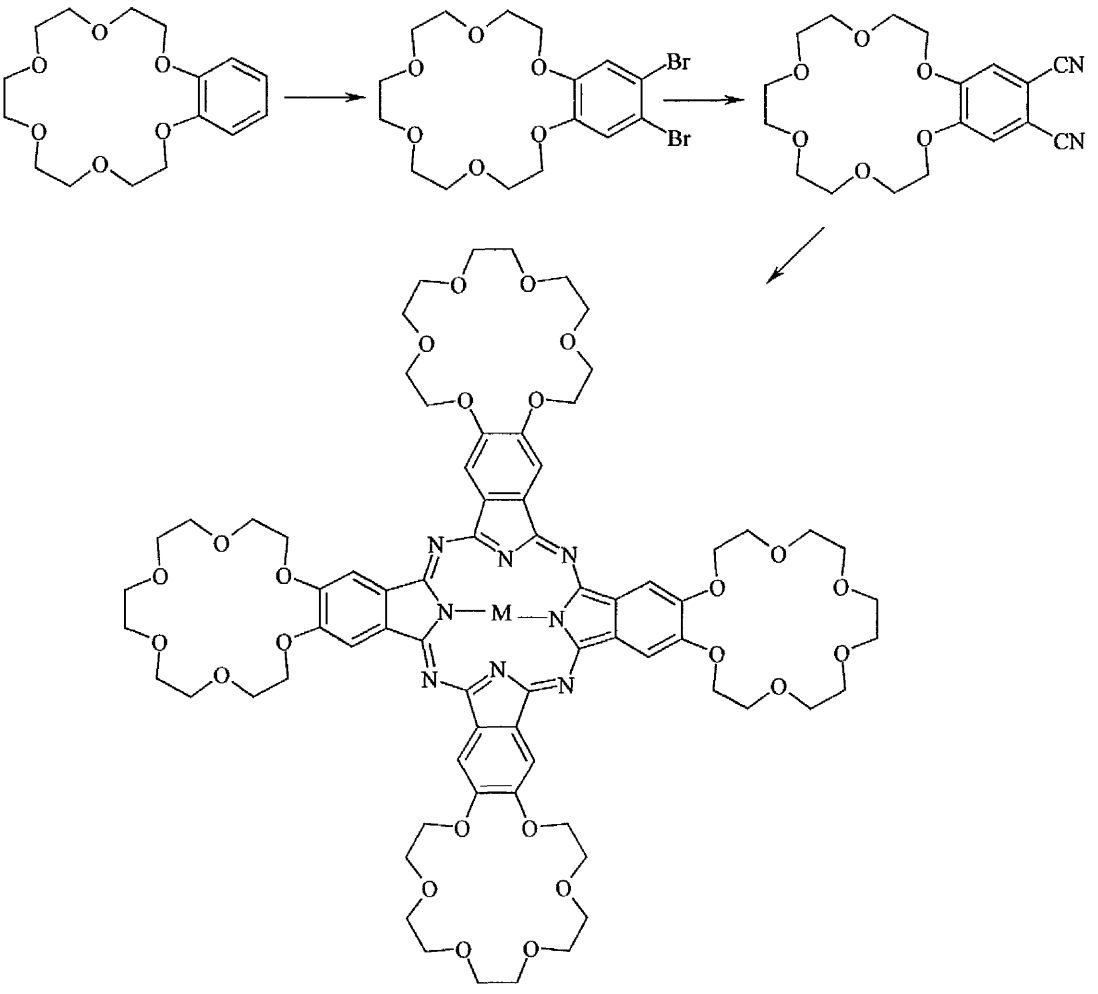


Figure 16: Pc crown ethers

This methodology has also been used to produce poly(ethyleneoxy)-substituted phthalocyanines[38b].

The synthesis of another peripherally substituted Pc - octa-cyanophthalocyanine - has been reported. Cyclisation of 1,2,4,5-tetracyanobenzene around a lithium template in refluxing propanol in highly dilute conditions, followed by aqueous hydrolysis gives the octa-cyano Pc[39]. Further hydrolysis gives the octa carboxylic acid, which can be transformed further to an octa ester or amide (Figure 17).

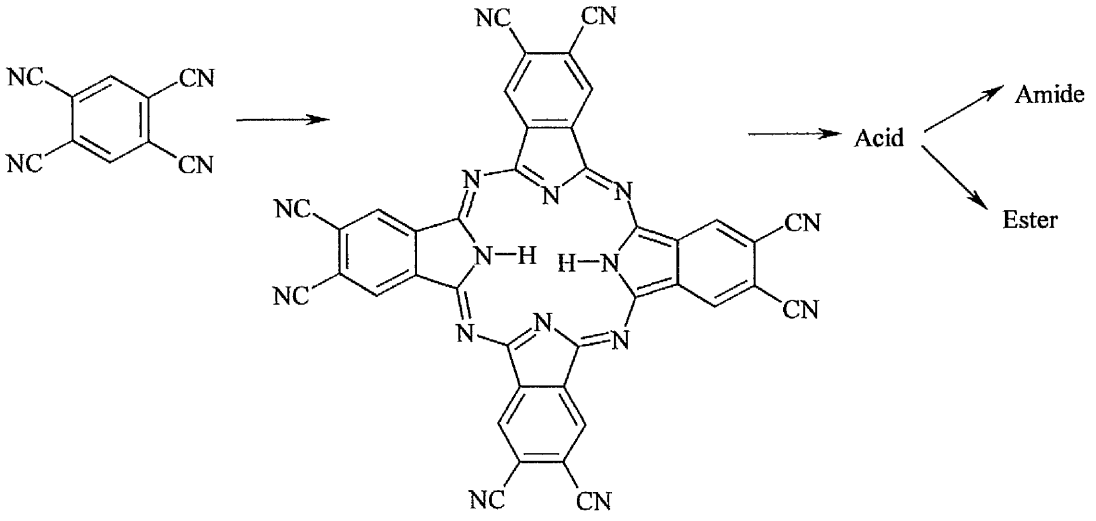
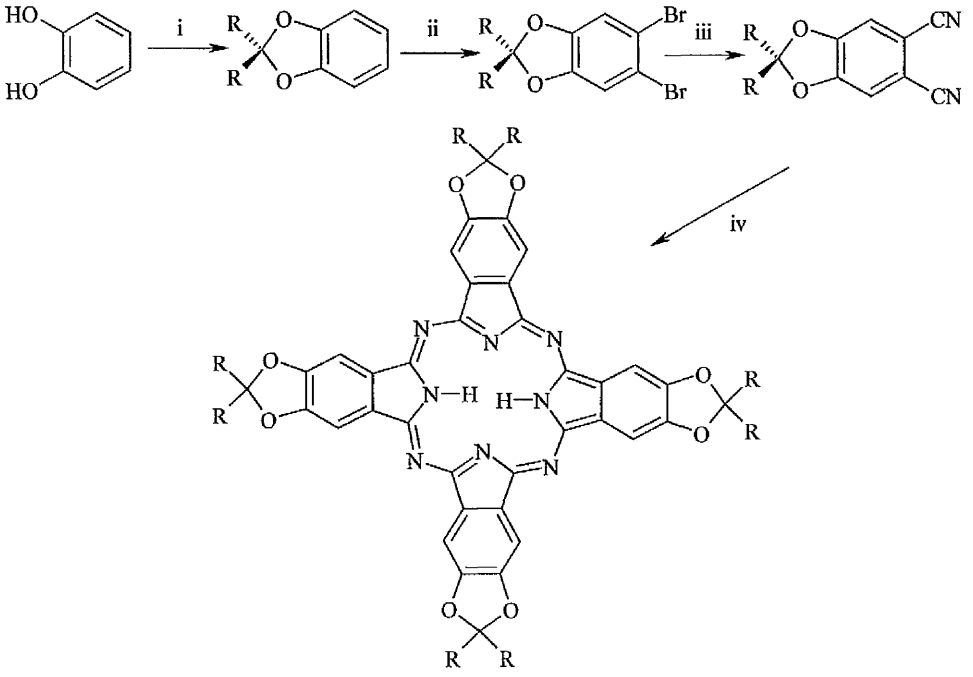


Figure 17: Route to octa-cyanophthalocyanine

Similar methodology to that described above has led to the synthesis of 'ketal' substituted phthalocyanines[40] (Figure 18).



i: Ketone, p-TsOH, Toluene, reflux; ii: NBS, DMF, RT; iii: CuCN, DMF;
iv: Li, PeOH, followed by aqueous hydrolysis

Figure 18: 'ketal' substituted phthalocyanines

Another recent development is the preparation of 3,4-daryl phthalonitriles via a Diels-Alder reaction[41] (Figure 19).

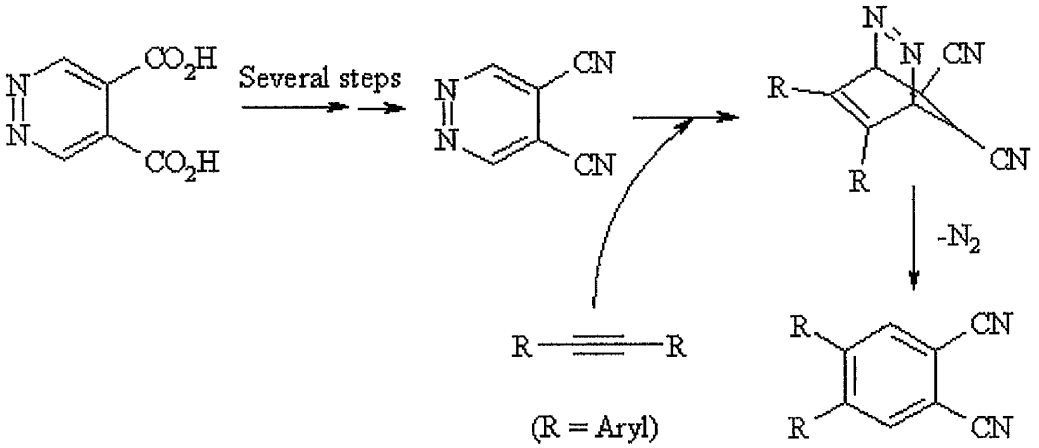


Figure 19: Formation of 3,4-diaryl phthalonitriles via a Diels-Alder reaction

The reaction of 3,4-dicyanopyrazine with di-substituted alkynes, followed by loss of molecular nitrogen generates a 3,4-diaryl phthalonitrile.

iv) Unsymmetrically substituted Pcs

The synthesis of unsymmetrically substituted phthalocyanines is of interest for various applications including the production of polymeric Pc, and the fabrication of Pc films. The synthesis of asymmetric phthalocyanines is usually achieved via a 'mixed' cyclisation of two phthalonitriles. For two different starting materials, there are theoretically six possible products as illustrated in Figure 20:

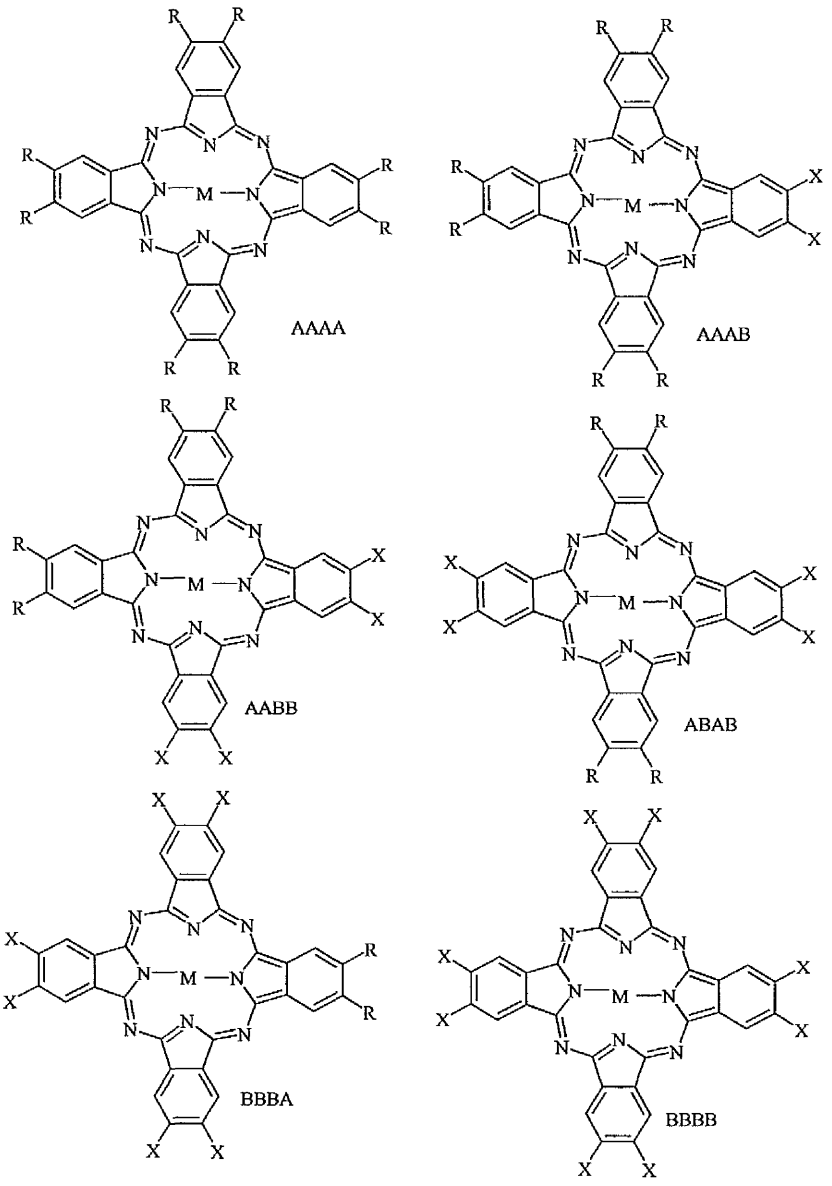


Figure 20: Products of 'unsymmetrical' Pc synthesis

The product Pcs can be denoted as AAAA, AAAB, AABB, ABAB, BBBA and BBBB types as illustrated. To a degree, control of the ratio of each Pc formed can be achieved by stoiciometric methods. Statistical analysis indicates a ratio of 3:1 would generate the best yields of the unsymmetrical Pc[42], however experimentally, it has been found that an excess of one reagent (at least 9:1) gives two main products – the AAAA and AAAB type. This method of synthesis requires sufficient difference in polarity between the two substrates to allow separation by chromatography.

An alternative method of producing asymmetrical Pcs has been by the use of a related macrocycle called a sub-phthalocyanine[43,44,45]. This type of structure contains only 3 isoindole units, and is formed by the cyclisation of 1,3-diiminoisoindoline molecules around a boron centre. This non-planar macrocycle can be reacted with a diiminoisoindoline to give an asymmetric Pc (Figure 21).

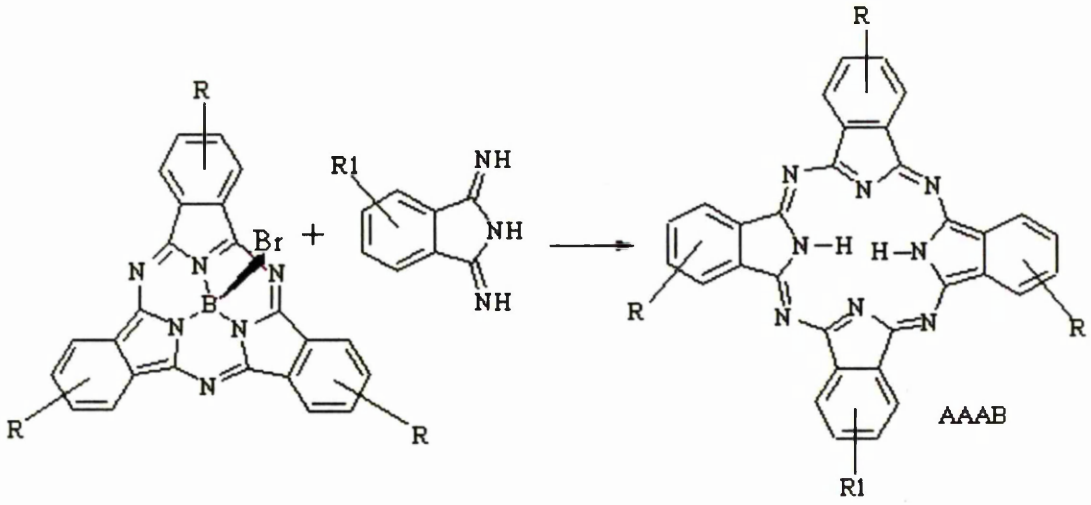


Figure 21: 'Unsymmetrical' Pc synthesis via sub-phthalocyanine

Relatively little work has been reported on the isolation of AABB or ABAB type phthalocyanines. One route of interest is the mixed cyclisation of 1,3-diiminoisoindoline with 1,3,3-trichloroisoindolenine[46]. The cyclisation of these two materials at room temperature apparently gives the ABAB type Pc almost exclusively in 5-7 % yields, however, whether the product Pc is the ABAB regioisomer, the AABB or a mixture has not been defined (Figure 22).

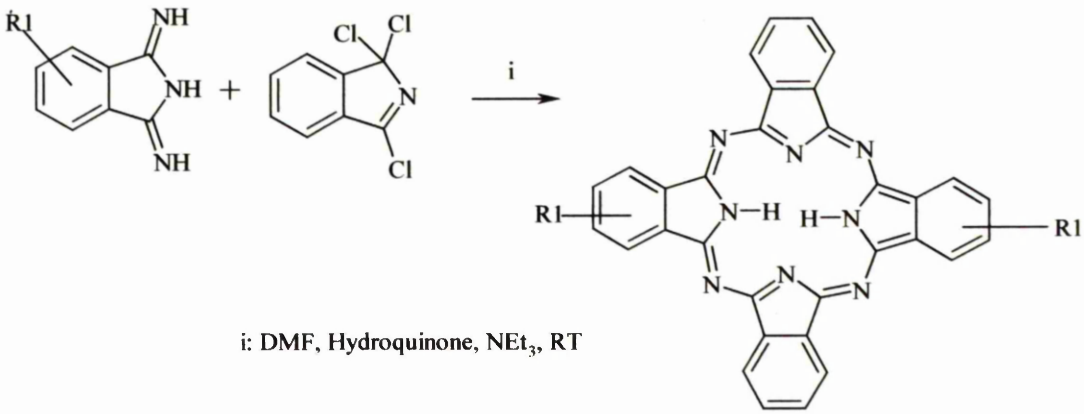


Figure 22: Unsymmetrical Pcs via mixed cyclisation of 1,3-diiminoisoindoline with 1,3,3-trichloroisoindolenine

Mixed phthalocyanine reactions have been used to facilitate the formation of several Pcs with varying properties including liquid crystalline Pcs, Pcs with macromolecular substituents, including dendrimers and poly(ethyleneoxides).

1.7: The Nature of π - π Stacking Interactions, and Their Impact on Pc Behaviour[47]

Non-bonding interactions between aromatic species are widely seen in many systems, both synthetic and biological. The overlap of adjacent multiple π (delocalised) orbitals underpin aspects of co-ordination chemistry, as well as in complex arrangements of bases in the formation of the DNA helix. This type of non-bonding interaction is an intrinsic feature of Pc behaviour in the solution state, and must be considered when attempting an understanding of the physical properties of phthalocyanines, whatever the final intended application of the material.

In solution, there are strong attractive interactions between Pc molecules. This aggregation effect leads to significant changes in the physical properties of the material, most noticeable in the UV-Visible and XRD spectra. Pcs adopt a co-facial arrangement of pairs or multiple molecules, 'π-stacking', with each stacking unit offset slightly off centre with

respect to its neighbours. The inter-molecular spacing tends to be approximately 0.34nm, (as measured by XRD), and the extent of aggregation controlled by a variety of factors. For example, aromatic solvent (e.g. toluene) or axial ligands on a metallated Pc can disrupt the 'self organisation', whereas choice of metal can increase the strength of the interaction. Effectively, the pyrrolic subunit of one molecule will sit directly above the central cavity (or metal in metallated species) of the adjacent molecule.

The effect of stacking on the physical properties of Pcs is varied. This 'self organisation' leads to the mesogenic properties of the liquid crystal Pcs, and is thus beneficial to that field of study. However, the close proximity of the aggregated molecules causes a dramatic change in the UV-Visible spectrum, resulting in a broadening of the normally sharp, 'definitive' Q-band peak at around 700nm. This leads to a poor chroma for colorants derived from the materials – the colorants are less intense in colour through the stacking of individual Pcs leading to 'exciton broadening'. This behaviour is caused by the molecular orbitals of closely associated molecules overlapping in the bulk material.

1.8: Phthalocyanine Solid State Behaviour

The crystalline properties of organic crystals differ in their origins from that of more traditional crystal structures. Whereas inorganic crystals acquire their properties through rigid covalent bonding, organic molecules – including crystalline Pcs – are formed through non-bonding intermolecular forces such as Van de Waals and π-π interactions. The result of these forces binding organic crystals is a flexibility of crystalline form termed polymorphism.

Planar unmetallated Pc and its metallated derivatives exhibit two common crystalline forms, the α and β polymorphs, with the β form more prevalent. This polymorph is usually described[48,49,50] as the most thermodynamically stable form of metal free and the essentially planar metal Pcs incorporating small cations, e.g. copper and zinc. The β form is a monoclinic crystal, belonging to the $P2_1/a$ space group, with two molecules per unit cell, and stacks of Pc molecules making an angle of 45° to 49° with the *b*-axis of the molecule[51]. The Pc stacks within the molecule are approximately at right angles to each other, giving a 'herringbone arrangement' (see Figure 23)[1].

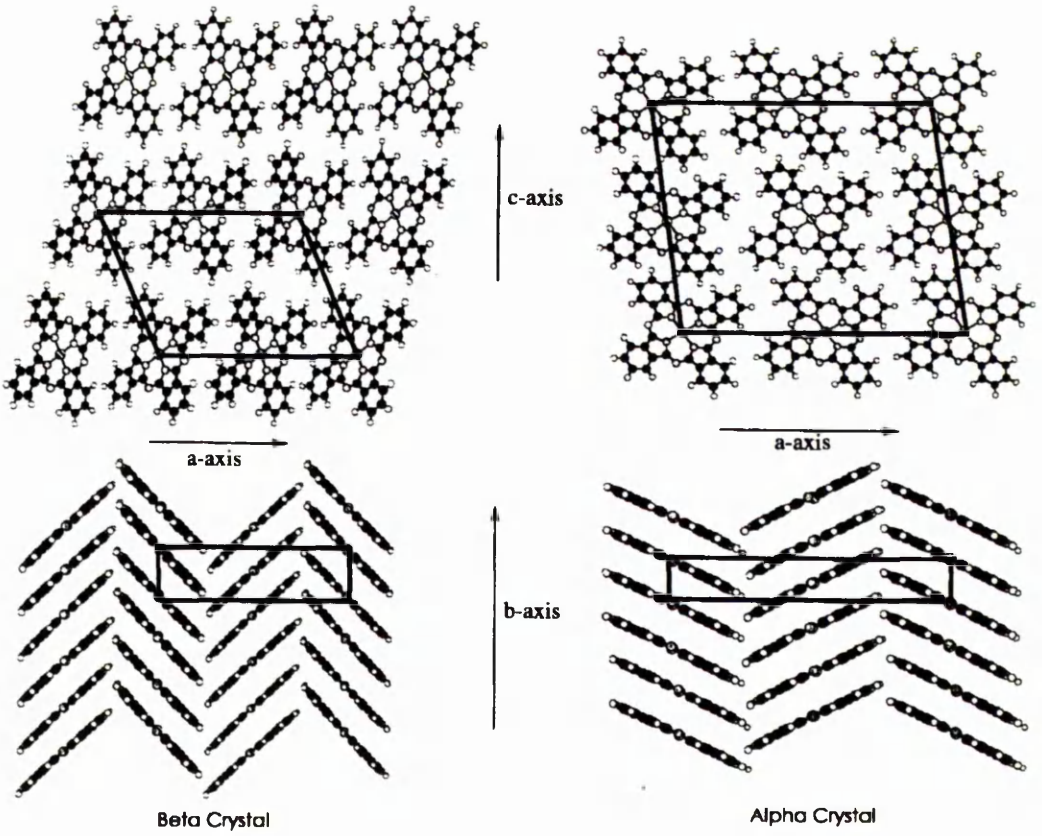


Figure 23: Pc Crystalline forms

The other common Pc polymorph, the α form, assigned C2/c space group, has a smaller tilt angle (27°-30°) than that of the β form[52,53]. This polymorph is seen in several Pcs, though

often the crystal size is too small to be useful for x-ray crystallography. The polymorph is often described as metastable, as heating above 200 °C irreversibly forms the β form.

1.9: Liquid Crystals[54]

The transition point of a molecular crystal (defined as crystalline by exhibition of three dimensional order) to a disorganised isotropic liquid through heating is termed the melting point of the crystal. Many materials undergo this process via various intermediate phases. The intermediate phases are described as 'mesophases' (meso = greek for intermediate), and some are liquid crystalline. Thus liquid crystals are liquids showing some degree of order

There are two sets of conditions where liquid crystal phases form: lyotropic materials can be formed by dissolving amphiphilic molecules in a polar solvent (usually water). The choice of polar solvent causes aggregation in the hydrophobic region of the molecule, and thus partial order in the solution state. This type of behaviour is observed in many commercial products such as detergents, and in biological systems such as cell membranes. The alternative condition in which LC behaviour is observed is in the pure material over different temperatures. Thermotropic liquid crystals undergo phase changes through either heating or cooling to or from the pure liquid (isotropic) state.

LC behaviour originates from the structure of the molecules themselves. LC materials are either 'rod like' (calamitic) or 'disk like' (discotic or columnar) in structure, and therefore have a rigid core with flexible exterior.

1.9.1: Calamitic LCs

Each calamitic LC phase is defined by the degree of order it exhibits: the lowest degree being nematic (N), showing simple positional order, followed by various smectic (S) phases, each showing different levels of layers of ordered structure (see Figure 24).

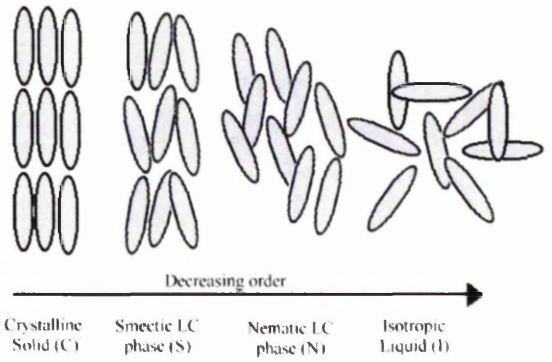
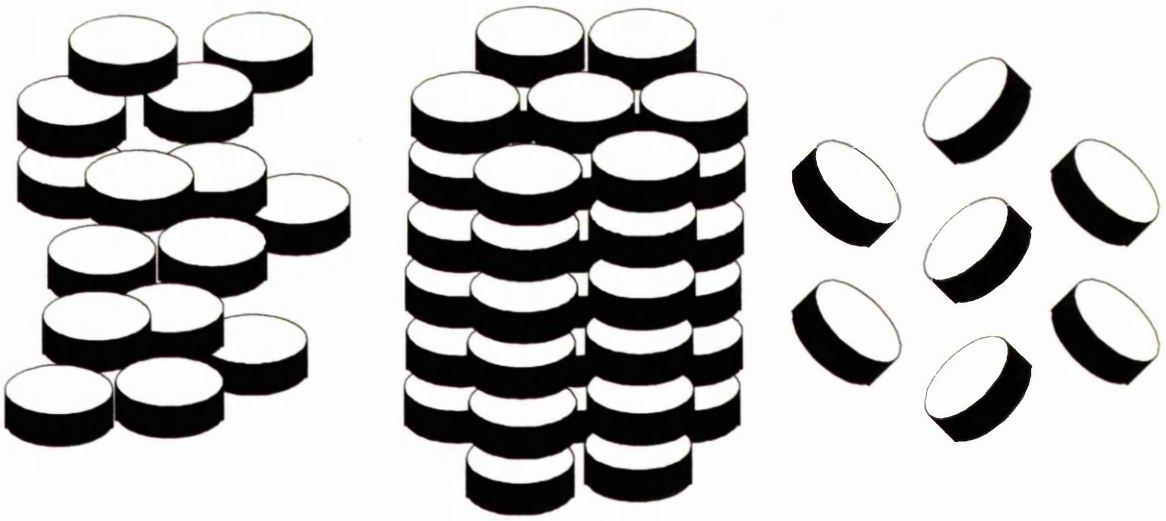


Figure 24: Calamitic crystalline phases

Identification of LC phases can be achieved via the individual birefringent texture exhibited when viewed under a light microscope fitted with crossed polarisers. The Nematic phase (Greek for 'threadlike'), exhibiting positional orientation of constituent molecules with respect to one axis, is seen as a series of threads on a coloured background. Both calamitic and discotic LCs can display nematic phases. Smectic mesophases are recognised for their 'soap like' appearance (Smectic = Greek for 'soap like'). However, unlike the nematic mesophases, the smectic phase exhibits polymorphism, and thus there are many different types of smectic phase.

1.9.2: Discotic LCs

Discotic mesogens[55] also exhibit nematic phases (N_D), but generally form hexagonal or rectangular columnar 'stacks' (see Figure 25).



i: Nematic (N_D) ii: Hexagonal columnar (D_h) iii: Rectangular columnar (D_r)

Figure 25: Discotic liquid crystals

The concept and theory of liquid crystalline behaviour was originally developed around the molecular architecture of calamitic LCs. Essentially, the calamitic mesogen consists of a rigid core with a flexible chain, generating the 'rod like' LC. In a similar fashion, the discotic mesogens have both rigid and flexible components to their molecular architecture. The disc like core of the molecule is a rigid structure, with peripheral flexible moieties attached to the core. Various classes of molecule lend themselves to the formation of discotic mesophases, with the rigid discotic core of the mesogen often being composed of polyaromatic species. The phthalocyanine molecule is one such example of this.

1.9.3: Liquid Crystalline Phthalocyanines[1]

The phthalocyanine molecule has a planar, rigid, aromatic structure, and thus tends to 'self-order' through π – stacking interactions. This aggregation effect leads to a variety of discotic mesophases, dependant on substituents[56,57], with various transition temperatures observed (crystalline – mesophases, mesophases – mesophases and mesophases – isotropic liquid). Several factors influence mesophase behaviour of Pcs: the number, type and method of attachment of flexible side chains; the length and branching of the chain, and the presence of chelated metal in the Pc core.

Generally, Pcs with four or fewer atoms in the flexible side chains would not exhibit mesophases, those with 'intermediate' chain length (four to eight atoms) will exhibit a crystal – mesophase transition temperature dependant on chain length, and chain lengths of more than nine atoms would lead to no clearly defined pattern in crystal – mesophase transition temperature. The transition from mesophases to isotropic liquid is also affected by increasing chain length in a similar manner.

Method of linkage of side chain also impacts on Pc behaviour. Typical linking moieties are alkyl (Pc-CH_2CH_2-alkyl), alkoxy (Pc-OCH_2 – alkyl), alkoxymethyl (Pc – CH_2O-alkyl) and alkyl-ester (Pc-CO_2-alkyl). The smaller steric interactions between adjacent relatively small alkoxy linked chains allow for the side chains to sit in the plane of the Pc ring – generating ordered hexagonal columnar mesophases. Crowded steric interactions between adjacent side chains on peripherally substituted Pcs linked with alkoxymethyl or alkyl

moieties tend to cause the formation of disordered hexagonal columnar or rectangular mesophases.

Steric effects are less relevant to non-peripherally substituted Pcs, and thus the electron donating or withdrawing effects of pendant groups on the π – stacking interactions of the Pc. Electron withdrawing groups stabilise mesophase formation, whereas electron donating groups have the opposite effect. Electron withdrawing substituents effectively make the molecule's σ – core more positive, increasing the attraction of the π – system of the adjacent Pc.

The central chelated metal ion (if present) can also influence the behaviour of a Pc mesophase. The increase in thermal range of the columnar mesophase is generally $Zn^{2+} > Co^{2+} \approx Cu^{2+} > Ni^{2+} > (H^{+})_2$. This relates to the increased π – stacking interactions of the metallated Pc due to the attraction of adjacent π – systems to the metal ion.

1.10: Background to Supra-Molecular Chemistry

The understanding of 'traditional' bonding, in the sense of covalent and ionic relationships between atoms has developed steadily since the inception of structural chemistry. Perhaps the most famous and thus generally understood example of supra-molecular chemistry via hydrogen bonding would be the Watson – Crick model of the assembly of the secondary structure of the DNA α-helix. From this groundbreaking theory comes the idea of 'molecular recognition' through non-covalent interactions[58].

The hydrogen bond is seen throughout chemistry as an interaction between a bound hydrogen atom and adjacent electronegative species. This is easily illustrated by a

molecule as simple as water, where each bound hydrogen exhibits a weak affinity to nearby oxygen atoms in other water molecules. This leads to unexpected physical properties such as the relatively high boiling point and indeed the liquid nature of the material itself at ambient temperature.

Of particular interest to the organic/biochemist are the bulk interactions of multiple hydrogen bonds within organic substrates (for example the Watson – Crick model as mentioned above). A thorough understanding of these interactions is essential when considering protein structure/folding and the behaviour of many biological processes. It would be perhaps inappropriate (and almost impossible) to attempt to summarise all of the observed organic/biochemical hydrogen bonded behaviour currently being studied here, but a brief explanation of the concepts behind the supra-molecular phthalocyanine chemistry would seem necessary.

1.10.1: Experimental Determination of Hydrogen bonds

Study of hydrogen bonding requires a subtly different approach to that of 'conventional' covalent structures. Whereas the covalent bond is formed via the movement of a significant amount of electron density away from the nucleus of the constituent atoms in the molecule through orbital overlap, the formation of the hydrogen bond only moves a small quantity of electron density. Consequently observed formation of the bond is seen through the change in physical properties of the substrate. The most straightforward qualitative method of testing for the presence of the bonds would be the 'gelling' effect of multiply hydrogen bonded mixtures of compounds in non-polar solvents[59]. For a more quantitative study, ^{1}H NMR, vibrational spectroscopy, x-ray diffraction, mass spectrometry and electron microscopy are possible techniques.

1.10.2: Two Component Hydrogen Bonded Systems

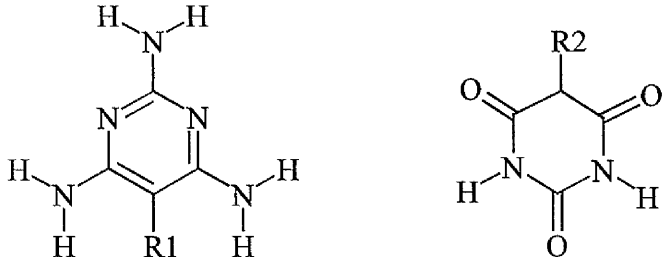


Figure 26: Two component hydrogen bonded systems

The 'self assembly' of pseudo polymeric species is based upon a repeating motif of complementary hydrogen bonded species. The two component system studied here is based on work published by Jean-Marie Lehn in 1990[60]. Lehn reported an unusual structure produced by mixing dialkyl barbituric acid (BA) and 5-alkyl-2,4,6-triaminopyrimidine (TAP). This mixture of two small molecules what appeared to be a polymeric species, and was shown to be a supra-molecular ribbon, or ladder polymer[61]. This could be best illustrated in Figure 27:

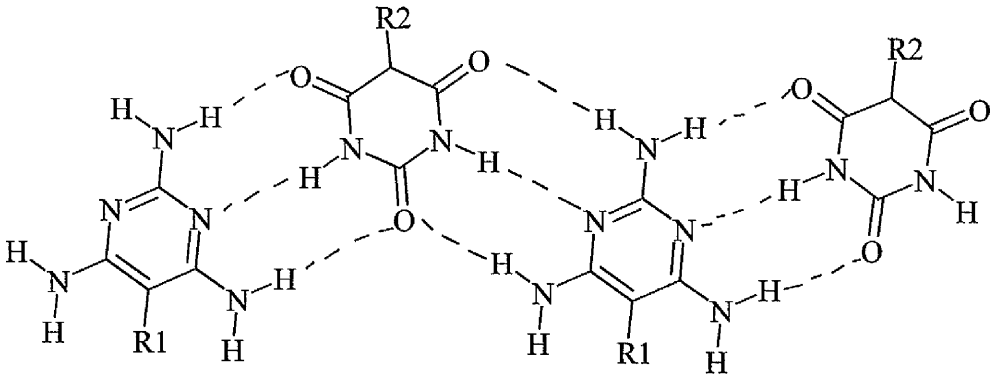


Figure 27: A hydrogen bonded supra-molecular ribbon

It was suggested that this type of structure could be the basis of a series of 'functional arrays' incorporating photo- or electro-active functionalities, then leading to applications in various fields such as catalytic, optical or electronic devices. More recently, several groups have concentrated on using multiple hydrogen bonded moieties to assemble pseudo

macromolecular structures such as cages, dimers and rosettes as precursors to various macromolecular structures.

One interesting structure reported by Lehn was the combination of the similar uracil functionality with TAP. By fusing two uracil subunits to a porphyrin ring and mixing the material with TAP, the synthesis of a self-assembling 'cage' dimer could be facilitated[61]. The central cavity generated in this way proved to be ideal as a host for certain small organic molecules. However, due to the free rotation of the uracil moieties, the cage structure existed in equilibrium with open 'zig-zag' oligomers.

The potential synthetic utility of this type of chemistry with phthalocyanines as the macromolecular component and BA derivatives as the 'linking' species was seen, and investigated.

1.11: Previous work

One approach considered to reduce the undesired aggregation effects of π-stacking has been the use of sterically hindered substituents to force molecules apart. Initial work consisted of attachment of substituents via a heteroatom, e.g. Figure 28[40]:

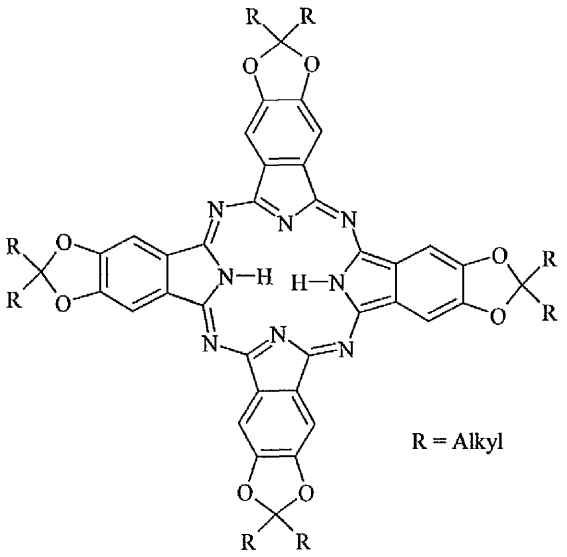


Figure 28: A 'ketal' Pc

This choice of methodology leads to two undesired effects – firstly the relative instability towards photo-induced degradation, but more importantly the shift of the UV absorbing Soret band into the blue region of the spectrum, resulting in a green Pc (thus inappropriate for cyan colorants). However, Pcs with 'ketal' functionality show good levels of 'disaggregation', leading to excellent UV behaviour.

1.12: Aim

A: Indane based compounds with long alkyl chains, branched side chains and bulky aryl substituents were predicted to significantly affect the extent of aggregation and solubility in organic or aqueous media of the resultant Pcs. Research was therefore initiated to synthesise suitable indane based monomeric units and observe the behaviour of the Pc derivative produced via the standard Pc tetra-cyclisation reaction. The overall strategy was to generate 8-substituted fused ring indanes and place nitrile groups at the 3 and 4 positions (Figure 29):

$R1 = C_nH_{2n+1}$ (n:6 - 12), CH_2Ar

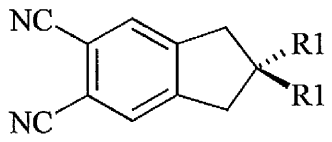


Figure 29: An indane based substituted phthalonitrile

The aggregation in solution of the resultant Pc could then be studied utilising UV spectroscopy, and any liquid crystalline behaviour studied via microscopy.

B: The core indane structure could be used as a base for Pcs designed with the capacity for further functionalisation. The introduction of ethyl ester moieties in the 8,8- position on the indane ring would allow synthesis of the octa ester Pc, octa acid and amide derivatives.

The utilisation of the methodology for the investigation of supra-molecular phthalocyanines could also be investigated. The previously reported work on porphyrin 'cage' structures could be used as an example to combine the known self assembly of the barbiturate – TAP motif with the π – stacking properties of phthalocyanine materials. The potential for supra-molecular 'ladder' pseudo-polymers could then be studied. Synthesis of an asymmetric Pc with 1,3-diethyl ester functionality could be followed by formation of the desired barbiturate and mixing with the TAP to attempt the creation of the supra molecular species (Figure 30).

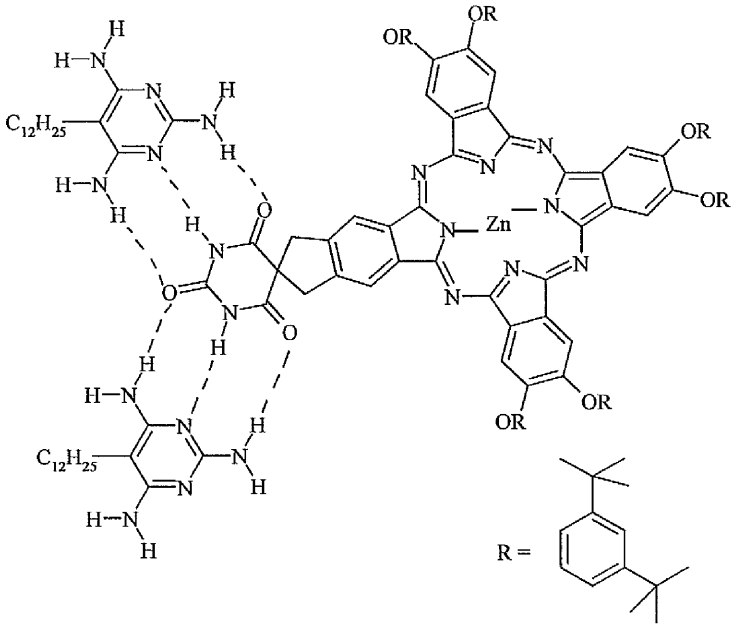


Figure 30: Pc supra-molecular chemistry

The presence of solublising alkyl groups would allow easier study of the final material, and the anticipated pseudo polymer would have the structure of a 'molecular zip' or 'ladder'as in Figure 31:

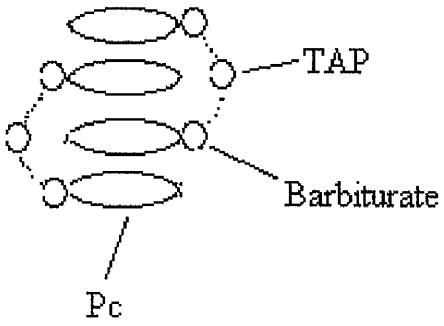


Figure 31: Pc 'ladder' pseudo polymer

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2.0: Synthesis of Indane Based Pcs with Alkyl and Aryl Side Chain Substituents

2.1: Alkyl Substituents

The overall aim of the project was the synthesis of indane based phthalocyanines with long alkyl and bulky aryl substituents

The first route considered was via alkylation of 1,3-indanedione (**1**)[62]. This was to be followed by reduction of the diketone to form the corresponding indane (**3**)[63, 64, 65, 66, 57]. Di-bromination of the indane moiety at the 3,4 positions would give the product (**4**), which could then be reacted with copper cyanide to give the desired phthalonitrile (**5**).

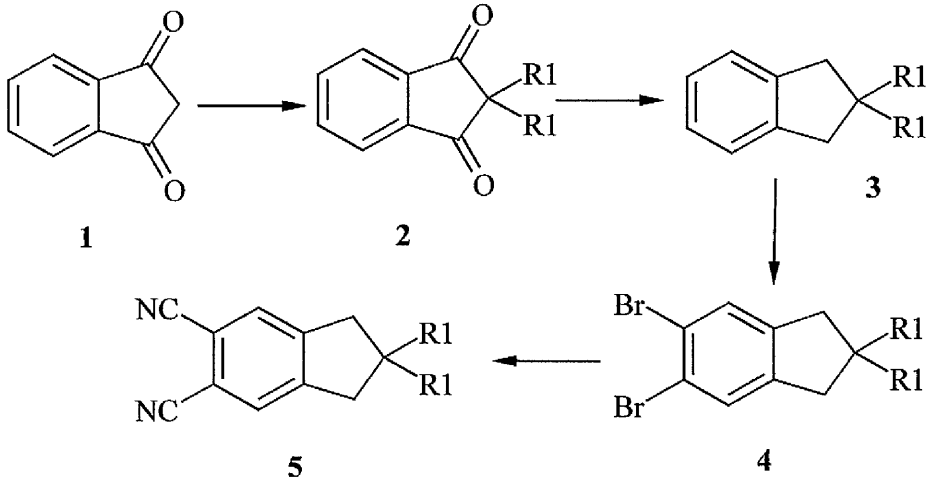


Figure 32: Route to desired phthalonitrile via 1,3-indanedione

The initial reaction involved dialkylation of 1,3-indanedione (**1**). This was first achieved using the base K_2CO_3 to remove the acidic protons α to the ketone functionality to form the enolate anion which would then react with an alkyl halide, in an S_N2 type reaction. Dialkylation would then form the di-alkylated indanone (**2**).

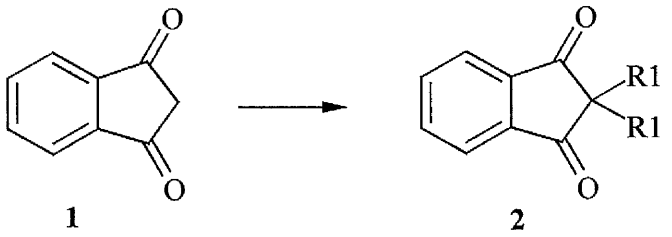


Figure 33: Dialkylation of 1,3-indanedione

This reaction proved to be low yielding with both the dodecyl iodide and bromide (22.2 % and 22.8 % respectively), and an alternative method was sought. The method chosen was a solvent mixture of 1:1 toluene and DMSO, and a change of base to KOH. This proved to be less successful that the original method (17 % with dodecyl bromide) and was abandoned.

Re-crystallisation of the crude di-alkylated material gave the desired product, which was then taken forward to the second stage of the synthesis. Various methods were attempted to try to reduce the ketone functionalities to the corresponding methylene groups to form the alkylated indane (**3**). The first and most obvious seemed to be the Wolff-Kishner[66] reaction. Wolff-Kishner type reactions have been demonstrated to reduce ketones α to aryl rings via formation and then reductive cleavage of hydrazones:

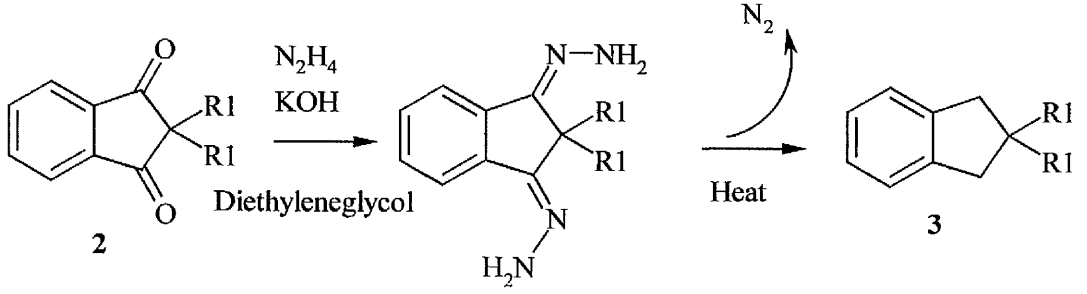


Figure 34: Wolff-Kishner reduction

The synthesis was attempted on a small scale to give the crude product, which was recrystallised from ethyl acetate. MS (EI) gave a molecular ion at e/z (M+H) = 496, possibly indicating the mono hydrazone:

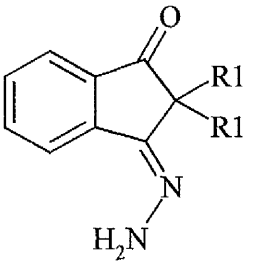


Figure 35: Mono hydrazone

Further attempts at forming the di-hydrazone and cleaving the C=N bond were made, changing solvent (DMSO) and base (KOtBu), but these proved unsuccessful, and finally this reaction was abandoned.

Published work suggested that an alternative method of utilising Wolff-Kishner type chemistry was available, by using tosyl hydrazones[67,68] as a replacement for hydrazine.

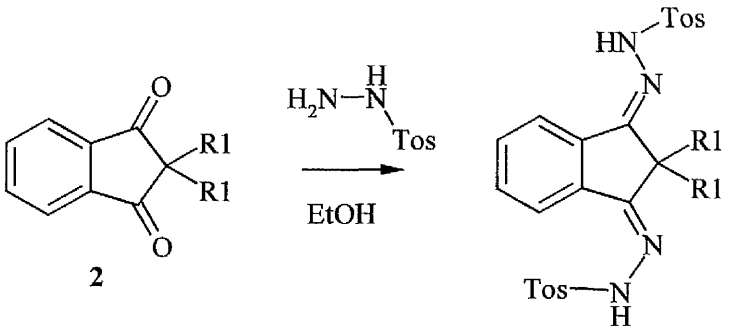


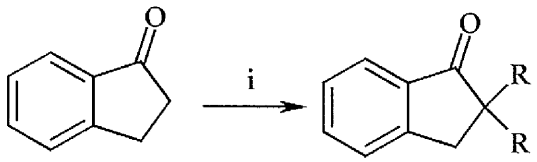
Figure 36: Wolff-Kishner type reaction with tosyl hydrazones

The hydrazide para-toluene sulfonyl hydrazide and the diketone (**2**) were refluxed in ethanol, but no evidence of reaction was seen via MS (EI/CI). The process was repeated using the higher boiling pentan-1-ol as solvent, but this yielded no evidence of hydrazone formation. The steric effects of the adjacent dodecyl groups are thought to be responsible for the lack of reaction. This, combined with the demonstrated low reactivity of the

substrate to the much smaller hydrazine monohydrate suggested that this approach should be discontinued.

Finally, following previous work on the reduction of similar ketones using triethylsilane as a hydride donor with a strong acid as proton donor (ionic hydrogenation), the diketone (**2**) was initially mixed with triethylsilane and trifluoroacetic acid (TFA) and refluxed in DCM[64]. This showed some evidence of reaction, but the reaction conditions were thought to be too dilute and the reaction was repeated using TFA as solvent. MS (EI/CI) showed slow reaction, and a stronger acid was considered. Trifluorosulfonic (triflic) acid was then used, with DCM as solvent[55]. Repeated additions of triethylsilane were required to drive the reaction, and this is thought to be due to the side reaction of the formation of triethylsilyl triflates. The reaction was demonstrated to work only partially, and the harsh conditions suggested that an alternative route would be desirable.

The difficulty of generating the alkylated diketone (**2**) from 1,3-indanedione (**1**) – very low yielding reaction – coupled with the extreme difficulty of the reduction step led to the consideration of an alternative approach. Previous work suggested that a strong base and an excess of alkyl halide could generate the desired di-alkylated product[63] (**7**) from 1-indanone (**6**).



6 **7**

i: RBr, KOtBu, toluene

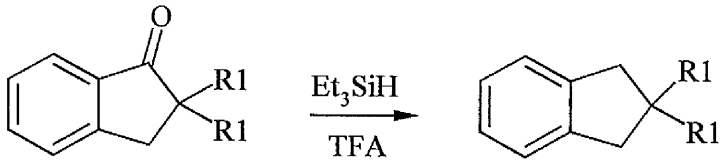
Figure 37: Dialkylation of 1-indanone

This reaction proved successful, and a number of 2,2-dialkylated indan-1-one derivatives were produced in reasonable yields as shown in Table 1.

Substrate R1	Yield %
7a $C_{12}H_{25}$	30
7b $C_{11}H_{23}$	91
7c $C_{10}H_{21}$	79.7
7d C_9H_{19}	91
7e C_7H_{15}	91.6
7f C_6H_{13}	91

Table 1: Yields for a series of alkylations

The reduction stage of the route was expected to be considerably easier to achieve with 2,2-dialkylated indan-1-ones by comparison to 2,2-dialkyl indan-1,3-diones. This indeed proved to be the case. The ketone (**7**) was dissolved in TFA and triethylsilane, and the mixture heated. Further additions of triethylsilane were required, presumably for the same reason as stated previously – formation of triethylsilyl trifluoroacetates. Yields proved to be acceptable, with an average of approximately 55 %, as illustrated in Table 2.



7 **3**

Figure 38: Ionic hydrogenation of 2,2-dialkylated indan-1-one with triethylsilane

Substrate R1	Equivalents TFA	Equivalents Triethylsilane	Time	Conversion %
3a $C_{12}H_{25}$	2	2	1 Day	<50
	3	3	2 Days	14.2
	4	8	3 Days	60.7
3c $C_{10}H_{21}$	EXCESS (21)	8	3 Days	55
3d C_9H_{19}	EXCESS (21)	8	3 Days	55.9
3e C_7H_{15}	EXCESS (36)	12	3 Days	28.2 *
3f C_6H_{13}	4	8	3 Days	56

*$BF_3.Et_2O$ (cat.) used to attempt to catalyse reaction

Table 2: Yields for a series of ionic hydrogenations of 2,2-dialkylated indan-1-one with triethylsilane

An alternative hydride donor was found in poly(methylhydrosiloxane). This was thought to be a cheaper source of the hydride anion. The reaction was thought to proceed in a similar manner to that using triethylsilane, but it was anticipated that the resultant poly(siloxanes) would be easier to remove from the reaction as solids. To some degree, this proved to be the case, though NMR evidence showed some smaller, liquid silanes present in the filtered material. Yields for this reaction were considerably lower than for those using triethylsilane (see Table 3), and the poly(siloxanes) proved more difficult to remove than expected. As a result, the reduction using triethylsilane was preferred.

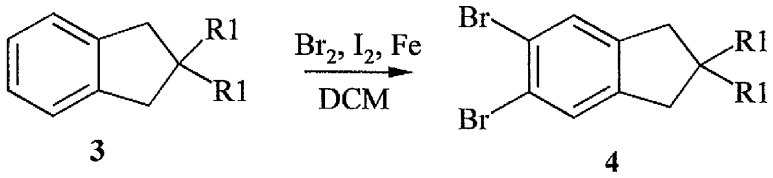
Substrate R1	Mmols. PHMS used	Yield %
3b $C_{11}H_{23}$	22	36.4
3d C_9H_{19}	20.6	28
3e C_7H_{15}	22.2	30
3f C_6H_{13}	3.3	58*

*Impure – large amount of poly siloxanes present.

Table 3: Yields for a series of ionic hydrogenations of 2,2-dialkylated indan-1-one with poly(methylhydrosiloxane)

The use of hydrogen and palladium on charcoal was then investigated (catalytic hydrogenation). Results indicate that this would be a better method of performing the reduction. Several ketones were treated to catalytic hydrogenation at standard temperature and pressure for four days. Purification via column chromatography gave the desired products as colourless oils in good yields. This methodology proved to be both higher yielding and cleaner than the ionic hydrogenation procedure, with none of the problems associated with the removal of excess silanes.

The bromination step of the synthesis proved to be unproblematic[72] (Figure 39). The reaction was catalysed with iron and iodine and the required 5,6-dibromo derivatives obtained in good yields.



3 **4**

R1 = $C_{12}H_{25}$, $C_{11}H_{23}$, $C_{10}H_{21}$, C_9H_{19}, C_7H_{15}, C_6H_{13}

Figure 39: Bromination of alkylated indanes

The cyanation stage of the synthesis was achieved using the Rosenmund-von Braun reaction. The displacement of the aryl bromides (**4**) in the indanes progressed with varying degrees of success. The reaction appears to be most successful when the reagents are heated to 160 °C quickly in a large excess of solvent. This avoids tetra-cyclisation around a copper template (the copper atom, once bound to the phthalocyanine is impossible to remove, and makes analysis by NMR difficult). Yields were low (see Table 4), probably due to the synthesis of the imide and copper phthalocyanine by-products. Purification was achieved via column chromatography, which removed insoluble copper complexes and by-products.

Substrate R1	Mmol.s Starting material	Yield %
5a $C_{12}H_{25}$	8.2	18.3
5b $C_{11}H_{23}$	7.2	25.0
5c $C_{10}H_{21}$	7.4	35
5d C_9H_{19}	8.35	39
5e C_7H_{15}	3.54	~100
5f C_6H_{13}	12.7	43

Table 4: Yields for the cyanation of a series of alkylated indanes

Metal free phthalocyanine (**8**) formation followed a standard method for this synthesis. A minimum amount of anhydrous pentanol was used as solvent for the tetra-cyclisation, using lithium as the metal template, followed by removal of lithium in methanol and centrifugation to isolate the solid Pc.

Substrate R1	Yield %
8a $C_{12}H_{25}$	7.4
8b $C_{11}H_{23}$	4.0
8c $C_{10}H_{21}$	8.4
8d C_9H_{19}	3.0
8e C_7H_{15}	4.0
8f C_6H_{13}	4.4

Table 5: Yields for the formation of a series of indane based Pcs

Yields for this step of the synthetic route were found to be very poor. This may be due to the substrate decomposing at the temperatures required to facilitate cyclisation.

The homologous series of phthalocyanines synthesised were of a deep blue/green colour. The Q – band of these Pcs were composed of a sharp pair of peaks at 660 and 700 nm, characteristic of non-aggregated metal-free Pcs.

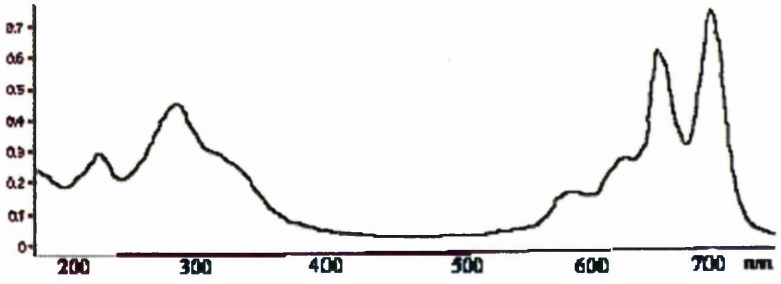


Figure 40: UV-Vis of unmetallated Pc

The materials were then studied via microscopy, and found, contrary to expectations, to exhibit both 'traditional' crystalline and liquid crystalline behaviour.

Crystalline substituted Pcs are often difficult to produce, due to the lack of order within the system caused by substituents disrupting intermolecular forces between molecules. Previous work with 'ketal' type Pcs had shown that alkyl substituents out of the plane of the Pc core forced adjacent molecules apart, reducing π – stacking and thus decreasing the order the system, removing any crystalline or LC behaviour. With the indane based alkylated Pcs, this was not the case. X-ray crystallography of the hexyl substituted derivative (**8f**) gave an insight into the likely reasons for this unexpected property:

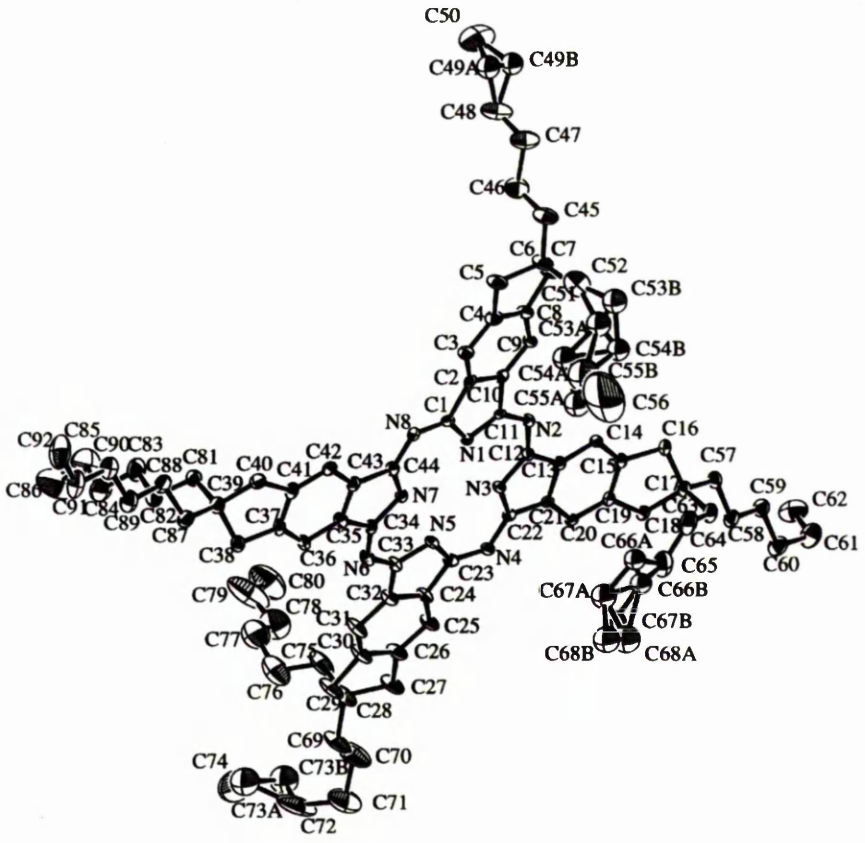


Figure 41: X-ray structure of hexyl substituted Pc 8f

The alkyl chains tended to 'fold' along the plane of the molecule rather than extend out of the plane of the core. This would not therefore force adjacent molecules apart, and explain the discotic mesophases seen using polarising microscopy. The crystalline packing of the molecule showed classic Pc behaviour, with the molecules forming a tilted β type arrangement. The hexyl derivative was seen to exhibit both crystalline and liquid crystalline phases.

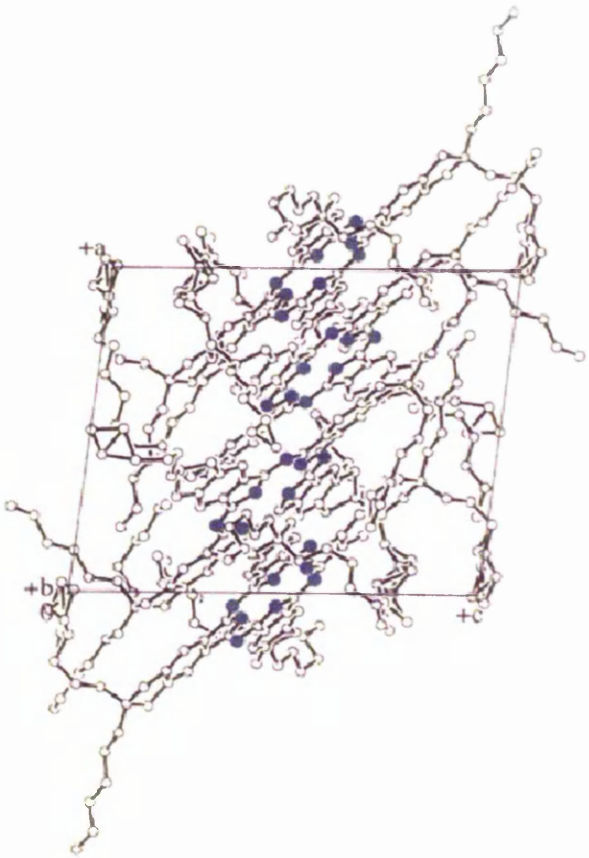
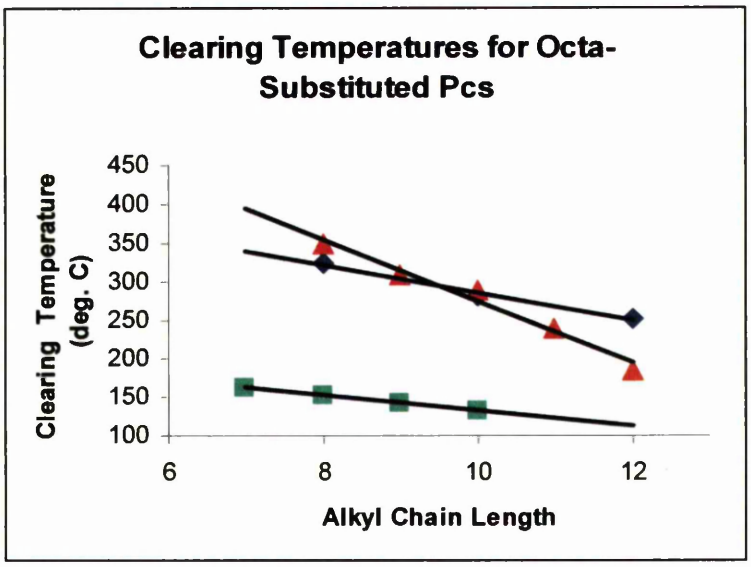


Figure 42: Crystal packing of hexyl Pc 8f

As noted, the indane based alkylated Pcs were seen to have thermotropic discotic mesophases. Their transition temperatures: crystal – mesophase (C – M) and mesophase – isotropic liquid (M – I) - were measured and compared to similar octa-alkyl substituted

Pcs.[70,71,72] Polarising optical microscopy observations were made using a heating plate, with the sample between two slides. All samples exhibited disordered hexagonal columnar mesophases.



Alkyl Chain Length	Non-Peripherally Alkylated H_2Pc (■)		Peripherally Alkylated H_2Pc (◆)		'Indane' H_2Pc (▲)	
	C – M (°C)	M – I (°C)	C – M (°C)	M – I (°C)	C – M (°C)	M – I (°C)
C_7H_{15}	113	163			160	Decomp.
C_8H_{17}	85	152	186	325	75	350
C_9H_{19}	103	142			*	310
$C_{10}H_{21}$	78	133	163	282	*	290
$C_{11}H_{23}$					*	240
$C_{12}H_{25}$			120	252	*	185

*Indistinct transition

Figure 43 and Table 6: Comparative clearing temperatures for alkylated Pcs

The heptyl derivative unfortunately decomposed before clearing, but the trend of decreasing clearing temperature with increasing chain length is clear. This is due to

isotropic transitions being a measure of the degree of order in the system. As chain length increases, then molecules are forced further apart, and so less energy is required to form an isotropic liquid. Substituents in peripheral positions have less impact on the discotic core of the molecule, and thus have higher clearing temperatures (more order) than molecules with substituents in non-peripheral positions. For the indane-based phthalocyanines the linkage of the alkyl chain encourages it to lie out of the plane of the macrocyclic core so that as the chain length increases it induces a more dramatic reduction in clearing temperature.

2.2: Substituted Benzyl Substituents

This methodology was then investigated further with a view to the attachment of bulky aryl groups on to the fused indane ring. The synthesis of 1-bromomethyl-3,5–di-tert-butyl benzene (**9**) was readily achieved via free radical bromination of 3,5-di-tert-butyl-toluene with NBS in good yield (85 %). Subsequent alkylation of the substrate 1-indanone proceeded using the methodology previously described, again in good yield (~ 100 %), (**10**).

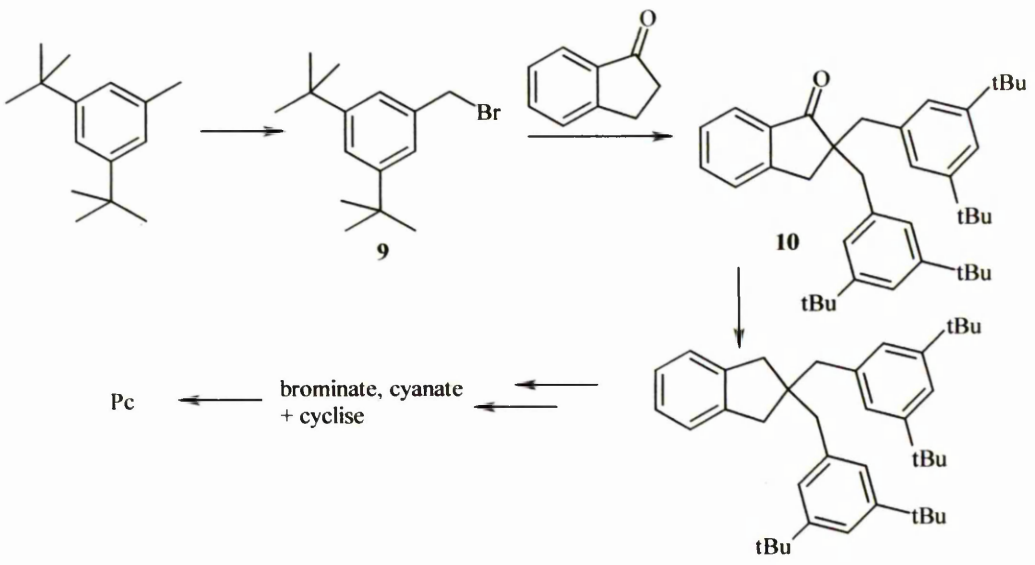


Figure 44: Scheme for the synthesis of indane based Pcs with benzyl substituents

The behaviour of this material was seen to be unusual by ^{1}H NMR spectroscopy. There appeared to be a difference in the behaviour of the benzylic protons. This is due to the protons closer in space to the electronegative oxygen of the carbonyl moiety being deshielded and thus downfield from those on the 'other' face of the molecule. The protons are thus intrinsically non-equivalent, and described as diastereotopic. As a result of the different environments of the protons 6a and 6b, the two peaks are split as a pair of doublets, rather than the expected singlet (see Figure 45).

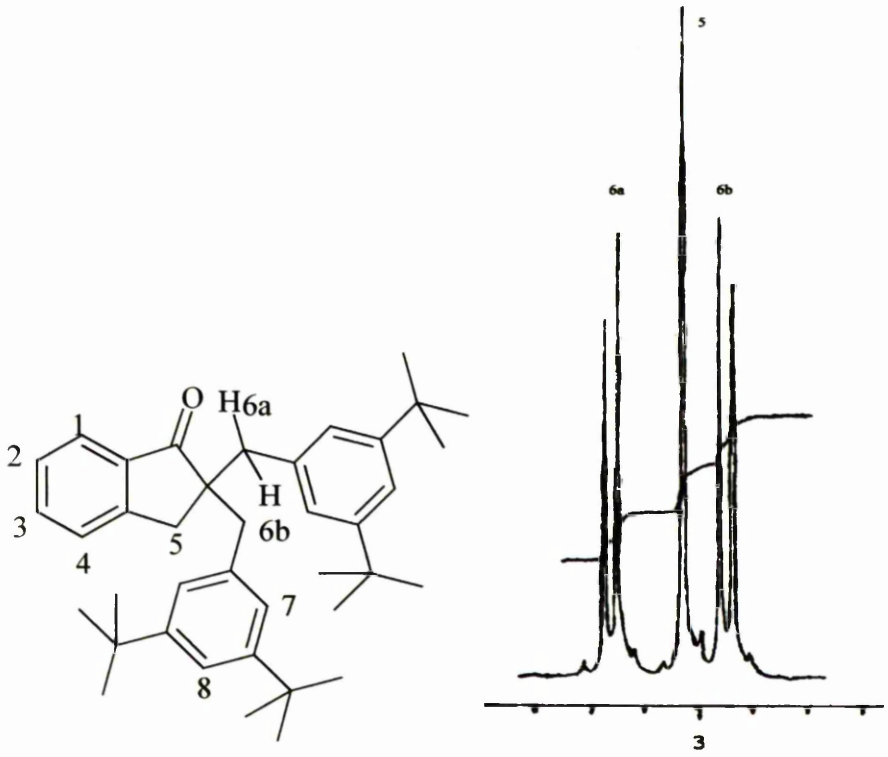


Figure 45: ^{1}H NMR spectral signals of hindered protons of dibenzylsubstituted indanone

Having observed this interesting effect, though allowing that the splitting would be lost on reduction of the ketone to the corresponding indane based ring system, the prospect of unusual behaviour in the resultant phthalocyanine were noted. However, this could not be investigated, as the very hindered carbonyl was extremely difficult to reduce. Both ionic and catalytic hydrogenation were attempted on the substrate, but attack of a hydride at the electron deficient carbonyl carbon proved impossible. The benzyl substituted indanone proved to be too hindered to reduce.

2.3: References:

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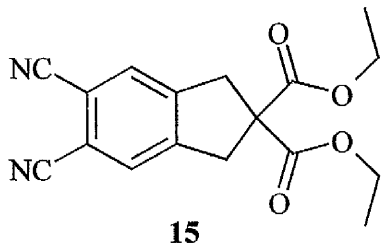
3.0: Synthesis of Indane Based Pcs with Ester and Amide Side Chain Substituents, 'Ketal' Type Analogues of Indane Esters: Towards Hydrogen Bonded Supramolecular Systems

3.1: Indane Based Pcs with Ester and Amide Side Chain Substituents

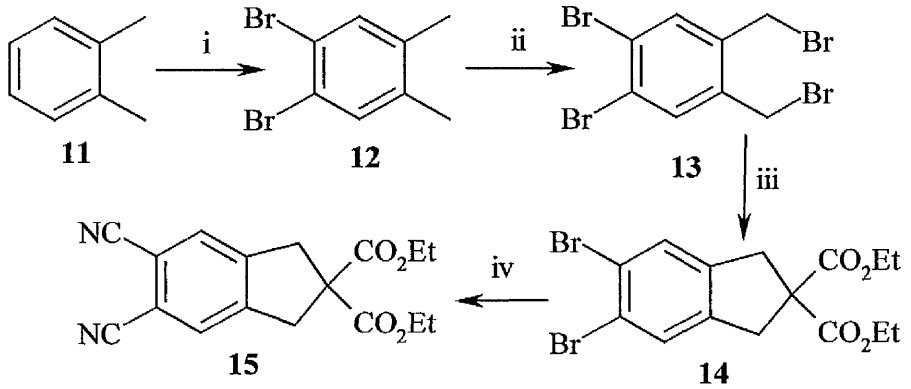
Following the synthesis of indane based Pcs with alkyl substituents, the capacity for further functionalisation was examined. In particular, the introduction of 1,3-diethyl ester moieties on the indane ring (Figure 46) could generate derivatives with highly polar groups and provide sites for further functionalisation. For example, transformations either before or after formation of the macrocycle could provide octa – acid, amides or alternative esters.



15

Figure 46: Diethyl 5,6-dicyanoindan-2,2-dicarboxylate

Synthesis of this type of molecule followed a different methodology to that previously described (Figure 47).



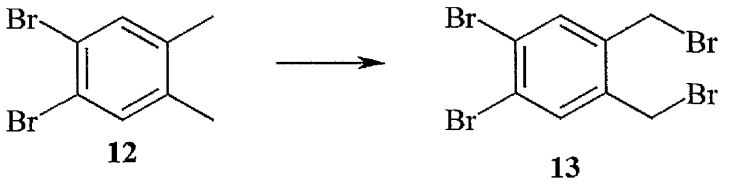
i: Br_2, I_2, Fe, DCM; ii: NBS, CCl_4, hv or $NaBrO_3$, $Na_2S_2O_5$, $EtOAc/H_2O$;
iii: $(EtO_2C)_2CH_2$, NaOEt, Et_2O; iv: CuCN, DMF

Figure 47: Scheme for the synthesis of diethyl 5,6-dicyanoindan-2,2-dicarboxylate

The initial step of the synthesis was the bromination of o-xylene[72,73,76](**11**), via previously reported methodology. Treatment of an ice cooled solution of the substrate in DCM with a solution of bromine (in DCM) with iron and iodine as catalyst over one hour was followed

by allowing the reaction mixture to warm to room temperature over three hours. Excess bromine was removed with sodium hydroxide solution, and the organics separated, dried and solvent removed to give the crude 4,5-dibromo-o-xylene as an oil, which crystallised on standing. Recrystallisation from methanol gave the desired material as a white solid (**12**). Yields were low (47 %), mainly due to the presence of mono and tri-substituted impurities, and difficulty in recovering the product from the recrystallisation solvent.

Two different synthetic approaches were attempted for the second step of the synthetic pathway. Previous work, including some in the group, had suggested that free radical bromination of 4,5-dibromo-o-xylene (**12**) with NBS in CCl_4 under a halogen lamp could effect the formation of the tetra bromide 4,5-bis(bromomethyl) 1,2-dibromobenzene[75] (**13**) (Figure 48).



12 **13**

Figure 48: Bromination of 4,5-dibromo-o-xylene

This was shown to be the case, in reasonable yield (57 %). However the presence of various impurities in the crude material caused problems in the purification step of the synthesis. Coupled with both the highly toxic nature and unreliability of supply of the solvent, an alternative method was considered.

Methodology was thus developed to utilise a mixture of sodium bromate and sodium metabisulfite as bromine source in an aqueous/organic two phase mixture, with ethyl acetate as organic phase[77]. Literature precedence suggested that four equivalents of each

reagent could be used, with sodium metabisulfite added as an aqueous solution dropwise to a vigorously stirred bi-phasic mixture of the substrate, dissolved in ethyl acetate and sodium bromate as an aqueous solution over about fifteen minutes, with the reaction mixture allowed to stir for four hours. Experimentally, it was found that this was not the case with the specific substrate used (Table 7), and so this methodology was expanded.

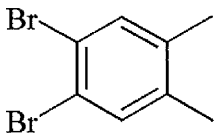
Substrate 	Quantity bisulfite added (equivs)	Quantity bromate added (equivs)	Reaction time (days)	Product ratio (mono/di substitution)
Run 1	2	4	1	~100/0
Run 2	4	4	2	~50/50
Run 3	4	8	3	~0/100

Table 7: Yields for the bromination of 4,5-dibromo-o-xylene

The reaction appeared to be driven by the mixture of the two aqueous reagents generating free bromine in small quantities to provide a bromine source. However, excess sodium bisulfite quenches the reaction, and thus control of rate of addition of this reagent is crucial for completion of the reaction. The successful transformation of the dibromide 4,5-dibromo-o-xylene **12** to the equivalent tetrabromide **13** under mild conditions was demonstrated in good yield, and the material generated taken on to the next stage of the synthesis.

The synthesis of the functionalised 1,3-diethyl 5,6-dibromoindan-2,2-dicarboxylate **14** was achieved through 'standard' enolate chemistry[78,79,80,81,82] (Figure 49).

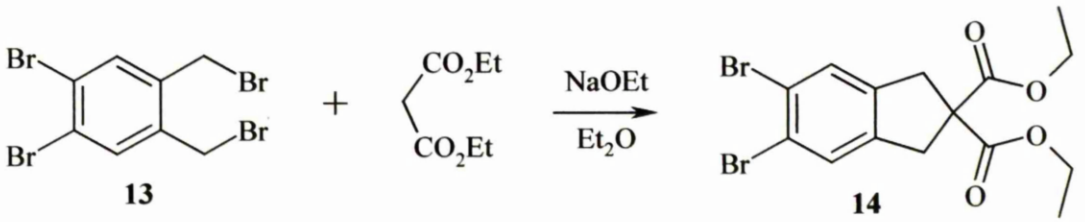


Figure 49: The formation of diethyl 5,6-dibromoindan-2,2-dicarboxylate

Dry conditions were found to be essential for the formation of the desired product in acceptable yields. It was found that both suspended sodium ethoxide, or base generated in situ were effective for the deprotonation of the diester. High dilution appeared to be important to avoid dialkylation of the bromide, and thus slow addition of the bromide was desirable. Yields were mediocre, and this is thought to be due to self-condensation of the enolate when formed, before addition of the bromide. The utility of the dual functionalised (both ester and bromide) molecule was then investigated.

Cyanation of the dibromide followed the standard 'von Braun' method, forming the phthalonitrile diethyl 5,6-dicyanoindan-2,2-dicarboxylate (Figure 50).

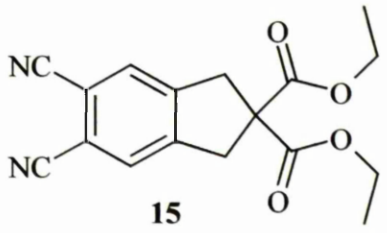
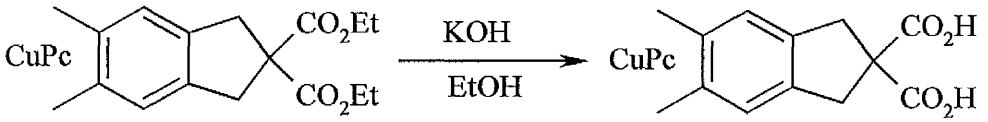


Figure 50: Diethyl 5,6-dicyanoindan-2,2-dicarboxylate

This reaction proceeded successfully, giving good yields of the desired phthalonitrile as a white solid. This material could then be cyclised to the phthalocyanine directly, or 'mixed' to make asymmetric species.

Direct cyclisation of the dibromide to form the resultant octa ester functionalised phthalocyanine (**16**) was also achieved using 'von Braun' methodology. Yields were low for this synthesis (5 %), but the Pc isolated was a deep blue material, with a characteristic sharp, non-aggregated Q – band in the UV-Vis at 678 nm. Saponification of this compound with potassium hydroxide in ethanol gave a Pc containing eight carboxylic acid moieties (**17**). The 'octa acid' Pc was shown to be sparingly soluble in warm water, and soluble in mild base.



16 **17**

Figure 51: Formation of octa carboxyl indane based Pc

Synthesis of the zinc centred octa ester (**18**) was achieved via cyclisation of diethyl 5,6-dicyanoindan-2,2-dicarboxylate (**15**), with zinc acetate as a template, in dry quinoline. As expected, this synthesis gave the deep green zinc phthalocyanine.

Various methods were attempted to further functionalise the octa – ester Pc to form the equivalent amide, either by the application of synthetic methodology on the phthalonitrile prior to cyclisation, or by direct reaction of the cyclised Pc. Initially, the functionalisation of diethyl 5,6-dibromoindan-2,2-dicarboxylate (**14**) was thought to be the most appropriate route for the synthesis of the desired target molecules[93,95,96,97,98,99].

Synthesis of a 1,3 – diamide was attempted via saponification of the ester and formation of the acid chloride. The 1,3-diacid (**19**) was formed in poor yield from the diester using standard methods. The acid chloride was synthesised by reflux in thionyl chloride and

used immediately to attempt to generate the amide by treatment with trityl aniline with pyridine as a base. This reaction was unsuccessful, possibly due to the hindered nature of the amine (Figure 52):

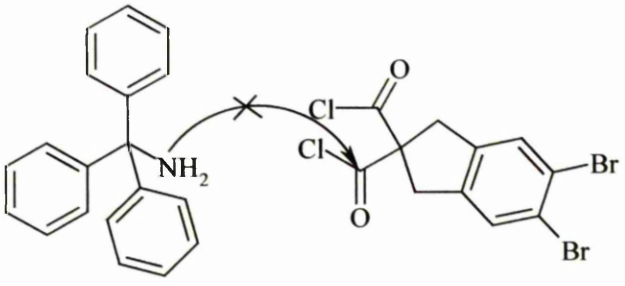


Figure 52: Attempted amidation of 5,6-dibromoindan-2,2-dicarbonyl dichloride

Or possibly the reaction conditions caused decarboxylation of the diacid (Figure 53):

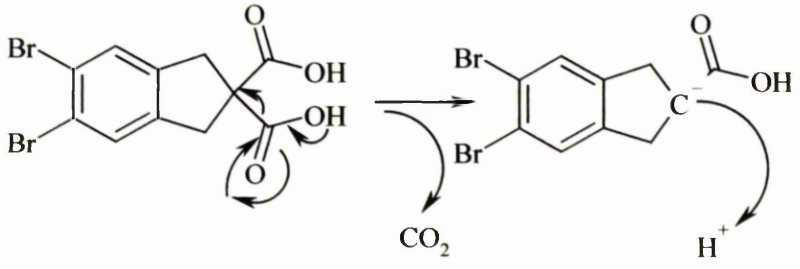


Figure 53: Decarboxylation of 5,6-dibromoindan-2,2-dicarboxylic acid

Identification of products proved difficult, and an alternative method was sought for this transformation.

The possibility of utilising a Lewis acid to catalyse formation of an amide was also considered[92]. References indicated that the direct transformation of an ethyl ester to an amide could be effected via the use of a Lewis acid catalyst in an aprotic solvent. The acid would activate the carbonyl of the ester moiety toward attack by a nucleophile such as an amine. This would thus generate the desired functionalised substituted indane.

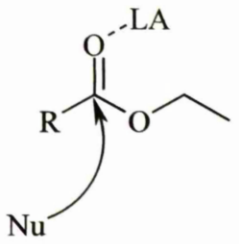


Figure 54: Lewis acid assisted nucleophilic attack on a carbonyl carbon

Association of the Lewis acid with the carbonyl pulls electron density from the oxygen, and this makes the sp^2 carbon more receptive to attack. Formation of an amide would be thermodynamically more stable than the ethyl ester starting material. However, experimentally, it was found that treatment of the diester with catalytic aluminium chloride in toluene, followed by addition of an amine did not generate the amide as expected.

The alternative approach to the formation of Pcs with amide moieties attached to the exterior of the molecule was to utilise the ester functionality on the preformed Pc. The copper centred octa acid Pc was chosen for this synthetic attempt. Conversion of the diacid **17** to the diformate ester was achieved to generate a better leaving group, and the ester treated immediately with hexylamine at reflux to generate the octa hexyl amide Pc[91] (**20**)(Figure 55).

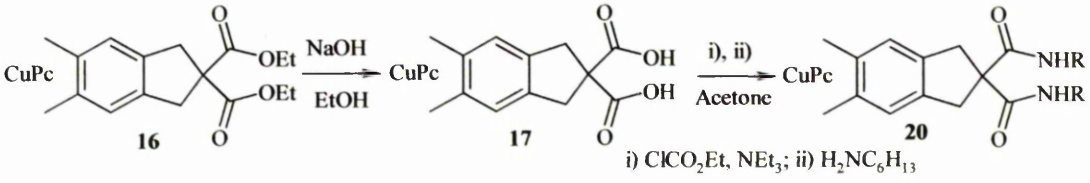


Figure 55: Formation of an octa hexyl amide Pc

The Pc formed was the definitive deep blue of a copper centred phthalocyanine, though unusually the material was an oil. The material was studied by MALDI mass spectrometry, IR and UV-visible spectroscopy. A single, sharp peak was seen in the IR at 3400 cm^{-1} indicating the presence of the single N-H stretch corresponding to the amide protons.

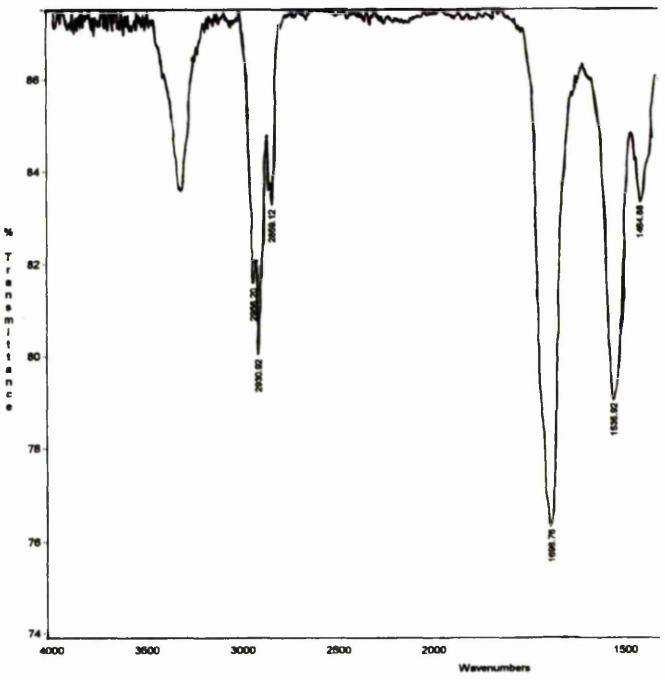


Figure 56: IR spectrum of an octa hexyl amide Pc

Analysis by UV-visible spectroscopy showed a phthalocyanine with a broadened Q – band characteristic of a highly aggregated material. This aggregation is probably due to intermolecular hydrogen bonding enhancing any π – stacking interactions between adjacent molecules.

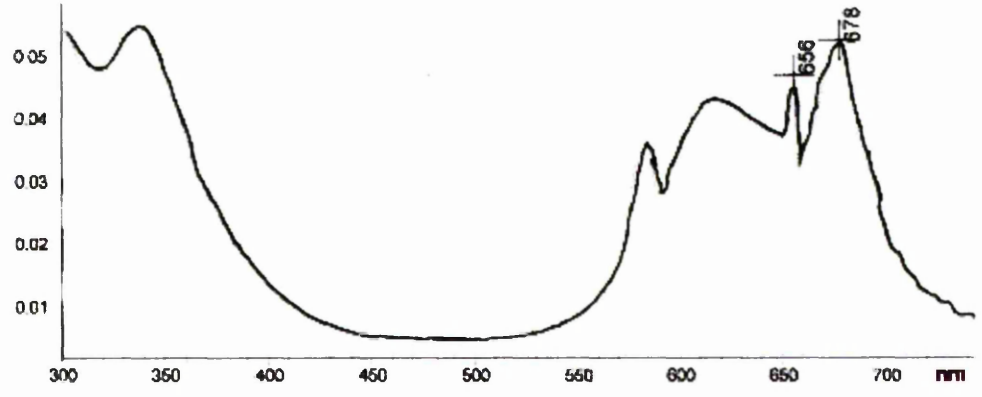


Figure 57: UV spectrum of an octa hexyl amide Pc

The methodology developed for the synthesis of diethyl 5,6-dibromoindan-2,2-dicarboxylate (**14**) was also applied for the synthesis of di-t-butyl 5,6-dibromoindan-2,2-dicarboxylate (**21**), with di-t-butyl malonate as the substrate for alkylation. (Figure 58)

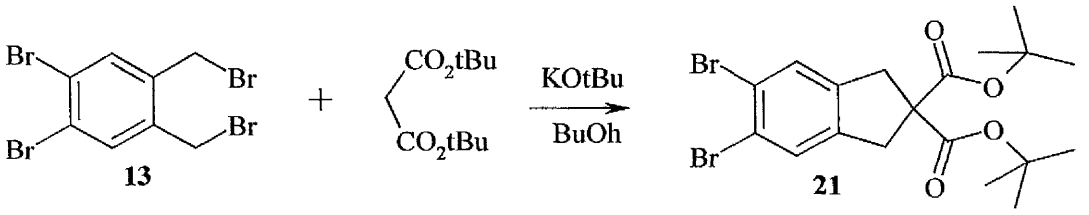


Figure 58: Synthesis of di-t-butyl 5,6-dibromoindan-2,2-dicarboxylate

Attempted cyclisation around a copper template (Rosenmund-von Braun reaction) proved unsuccessful, and the route abandoned in favour of considering transesterification on the preformed diethyl ester functionalised phthalocyanine.

3.2: 'Ketal' Type Analogues of Indane Esters

Following previous work on 'ketal' type Pcs with aliphatic substituents, the synthesis of 'ketal' analogues of the ester functionalised indane based phthalocyanines was thought appropriate, as it was anticipated to be similar in physical properties with the 'ketal' Pcs with aliphatic side chains and allow for comparison with the 'indane ester' phthalocyanine and its derivatives.

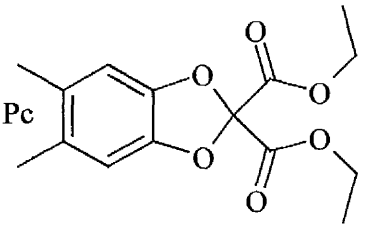
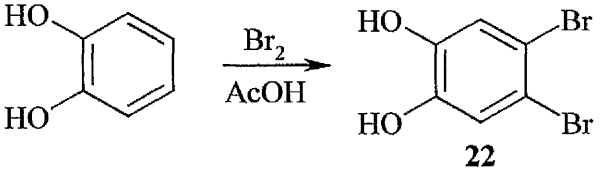


Figure 59: Pc derived from diethyl 5,6-dicyanobenzo[1,3]dioxole-2,2-dicarboxylate

Initially it was thought that the synthetic approach should involve the preparation of the ketal dibromide[86], followed by cyclisation around a copper template (Rosenmund-von Braun reaction) to give the copper phthalocyanine. As the shortest route, this would give the quickest insight into the physical properties of the resultant material. The route decided upon was via 5,6-dibromo catechol, readily synthesised from reaction of catechol with elemental bromine in good yield (64.2 %) (Figure 60).



22

Figure 60: Synthesis of 5,6-dibromo catechol

Treatment of the dibromide **22** with dibromo diethyl malonate[85] gave the desired 'ketal' type species with both ester and aryl dibromide functionality (**23**). Yields were poor (34 %), possibly due to side reactions with the solvent (acetone).

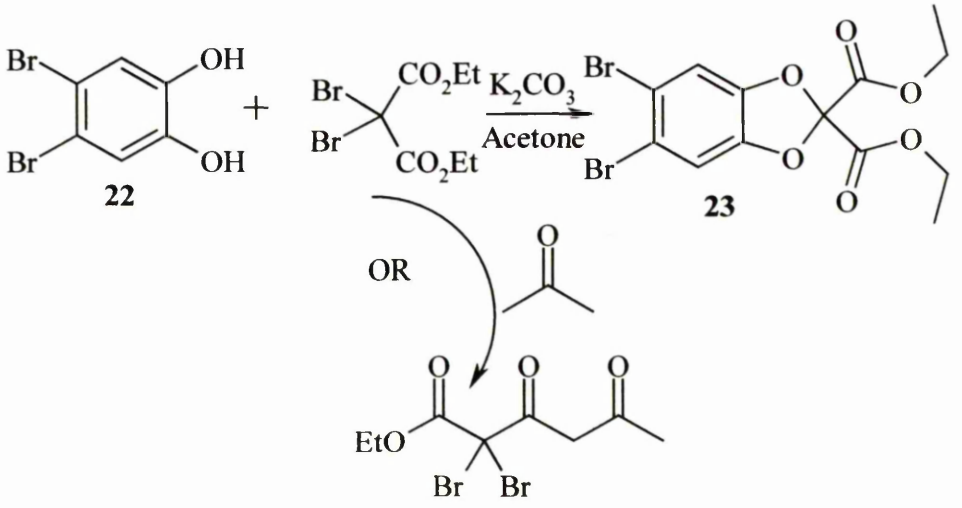


Figure 61: Possible side reactions in the formation of Diethyl 5,6-dibromobenzo[1,3]dioxole-2,2-dicarboxylate

Direct cyclisation of the dibromide **23** around a copper template proved unsuccessful. This was thought to be a result of the harsh conditions required for the Rosenmund-von Braun reaction destroying the substrate. An alternative procedure was thus sought.

As an alternative method, the formation of 5,6-dihydroxy phthalonitrile[83,84] (**24**) and subsequent reaction with dibromo diethyl malonate[85] could lead to formation of a functionalised phthalonitrile (**25**) (Figure 62).

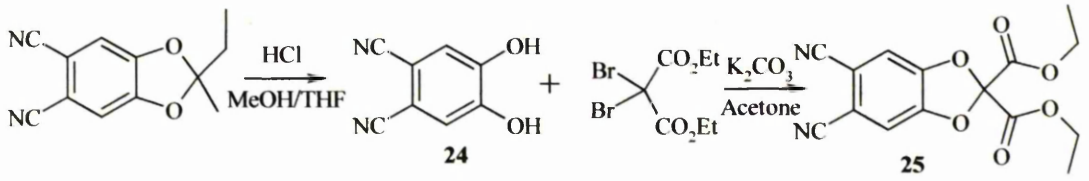


Figure 62: Scheme for the synthesis of diethyl 5,6-dicyanobenzo[1,3]dioxole-2,2-dicarboxylate

This compound could then be cyclised to form the Pc templated around zinc or lithium. Conditions for the zinc acetate – quinoline method would be harsher that for lithium –

pentanol, but the latter method, thought milder could potentially result in transesterification of the 1,3-diethyl ester moiety on the substrate to the 1,3-dipentyl ester (Figure 63).

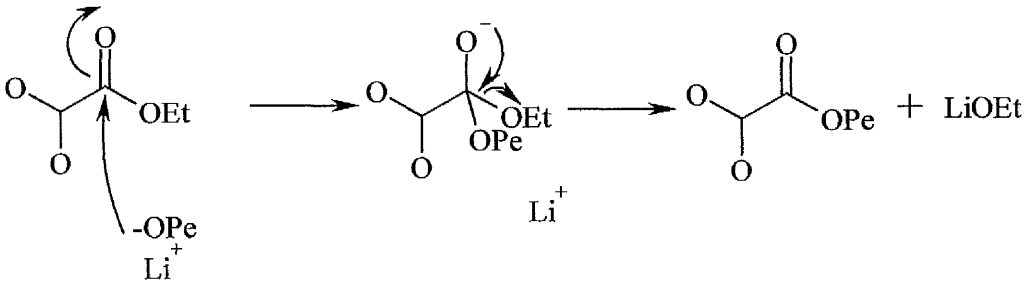


Figure 63: Transesterification of ethyl esters

Synthesis of the phthalonitrile **24** was achieved via acid hydrolysis of the methyl-ethyl ketal. Introduction of the 1,3-diethyl ester moiety was then achieved utilising the methodology previously described for the dibromide, with purification via column chromatography.

Both the zinc acetate – quinoline and lithium – pentanol methods were attempted, and no evidence of phthalocyanine formation was seen. It was concluded that that the ketal – ester functionality was too thermally unstable for phthalocyanine formation to be viable.

3.3: Hydrogen Bonded Supramolecular Systems

Having established the methodology to synthesise indane based phthalocyanines with diethyl ester substituents, it became possible to explore the possibilities offered by the combination of the known π – stacking aggregating behaviour of phthalocyanines and the reported synthetic utility of the barbiturate (BA) and triamino pyrimidine (TAP).

The π (delocalised) system of the phthalocyanine molecule tends to exhibit strong non-bonding interactions with adjacent molecules through the behaviour termed 'π – stacking'. This leads to interesting physical properties; some beneficial, such as the semi-ordered LC behaviour, some less so e.g. exciton coupling in aggregated Pcs giving broad peaks in the UV-Visible spectrum and thus poor chroma for ink jet colorants. It was thought that utilising this property, and then re-enforcing this by functionalising an asymmetric Pc to include a barbituric acid moiety and mixing the resultant Pc with TAP, a 'molecular zip' ladder pseudo polymer could be generated.

The synthesis of a model barbiturate to investigate the hydrogen bonding behaviour of the barbiturate-TAP mixture was achieved using similar methodology to that employed to form diethyl 5,6-dibromoindan-2,2-dicarboxylate. Using 1,2-bis(bromomethyl) benzene as a starting material, treatment with diethyl malonate gave the analogous compound diethyl indan-2,2-dicarboxylate (**26**). Reaction of the resultant 1,3-diethyl ester moieties with urea in the presence of sodium ethoxide as a base then generated the desired model barbiturate[87,88,89,89,90,91,92] (**27**). The amide protons can be seen by NMR as illustrated (Figure 64).

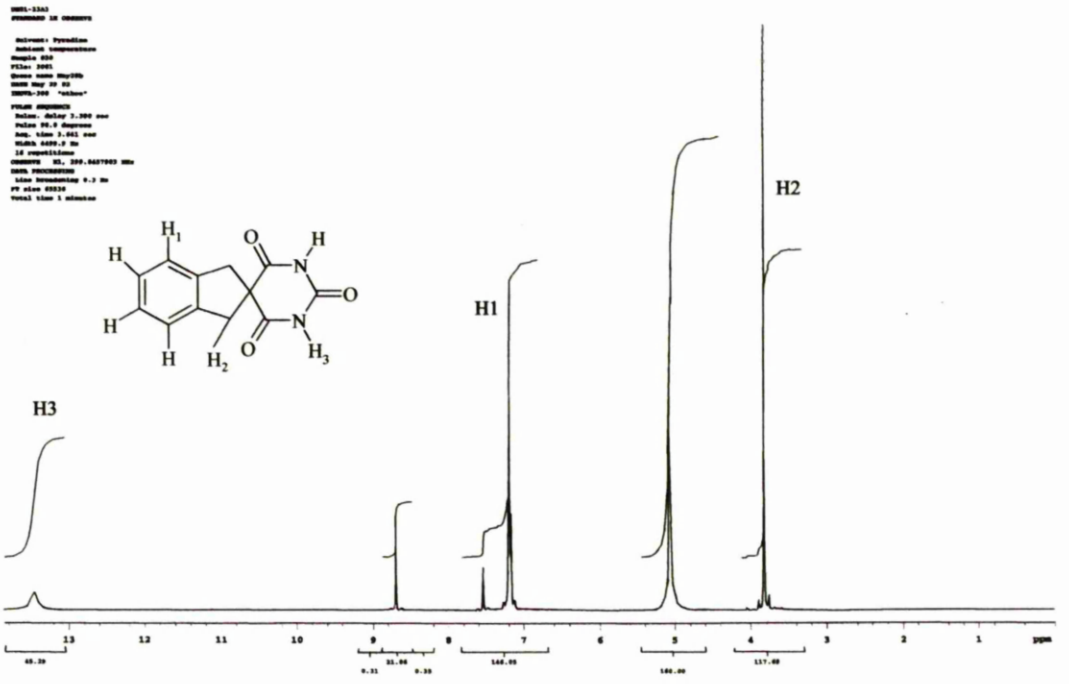


Figure 64: ^{1}H NMR spectrum of (5-indan) barbituric acid

The material was then mixed with 5-dodecyl-2,4,6-triaminopyrimidine and heated in chloroform until both materials dissolved. On cooling, a gel was seen to form, indicative of the formation of strong hydrogen bonds.

Analysis of the material 5-dodecyl-2,4,6-triaminopyrimidine by ^{1}H NMR (300 MHz, d_5-pyridine) indicated that the protons attached to the amino moieties on the pyrimidine ring could be seen at 6.08 and 6.26 ppm (s, 2H and s, 4H respectively) (Figure 65).

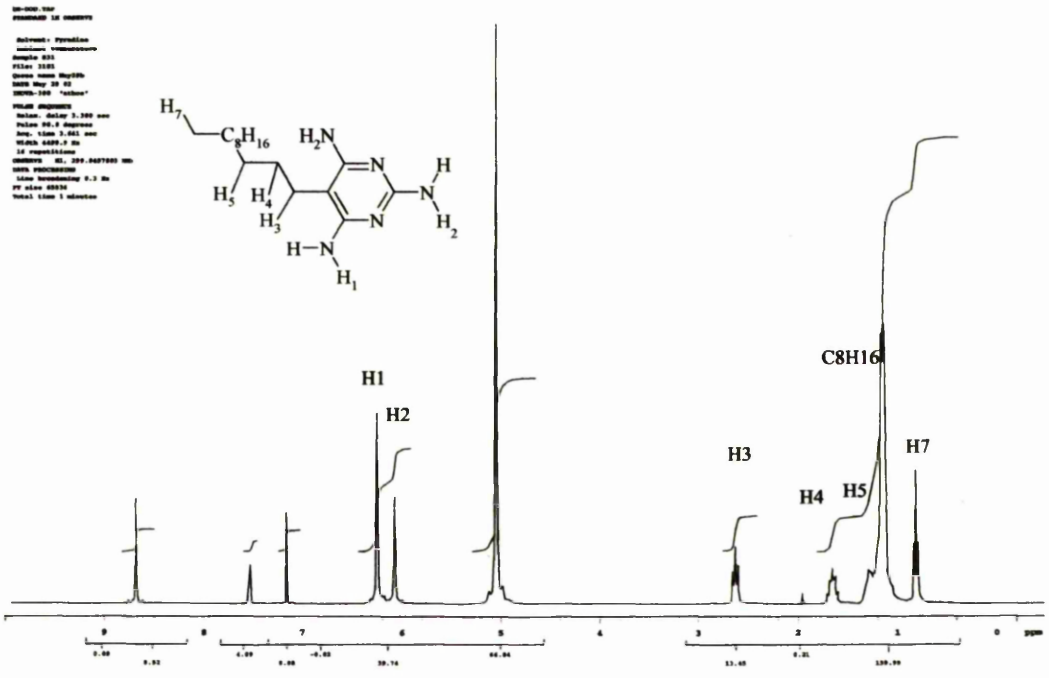


Figure 65: ^{1}H NMR spectrum of 5-dodecyl-2,4,6-triaminopyrimidine

As a qualitative measure, the formation of a gel is indicative of the presence of hydrogen bonding. The effect of such non-bonding interactions on NMR behaviour was thought to shift the peaks corresponding to the barbiturate and amino protons, as hydrogen bonding would de-shield the nucleus of each proton.

The gel formed from a mixture of the two materials in chloroform was heated under reduced pressure to remove the solvent, and the mixed residue was studied by NMR, under the same conditions as for the two materials individually.

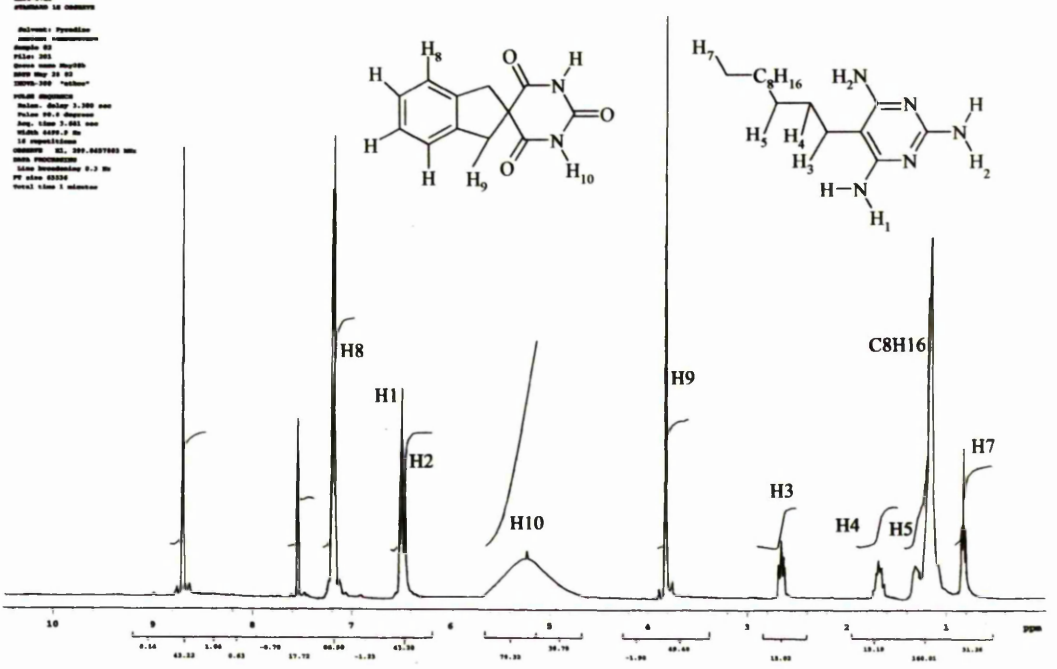


Figure 66: ^{1}H NMR spectrum of TAP and barbiturate derivative

The effect of hydrogen bonding between the barbiturate and TAP functionalities can be clearly seen by the positions of H1 and H2 (Figure 66). These protons are deshielded, and their peaks shifted towards 10 ppm. The hydrogen bonded protons can be seen at 6.46 (s, 2H), 6.49 (s, 4H) ppm. It was thus demonstrated that NMR would be appropriate technique to use as an indicator of the formation of hydrogen bonds.

The synthesis of an asymmetric Pc with barbiturate functionality was therefore attempted. The phthalonitriles diethyl 5,6-dicyanoindan-2,2-dicarboxylate (**15**) and 4,5-bis-(3,5-di-tert-butyl-phenoxy)-phthalonitrile (supplied by the McKeown group)[100] were mixed in a ratio of 1:3 in dry quinoline, and cyclised around zinc (present as zinc acetate) to form a mixture of Pcs – primarily the octa phenoxy Pc, but also the 'AABB', 'ABAB' and the desired asymmetric Pc.

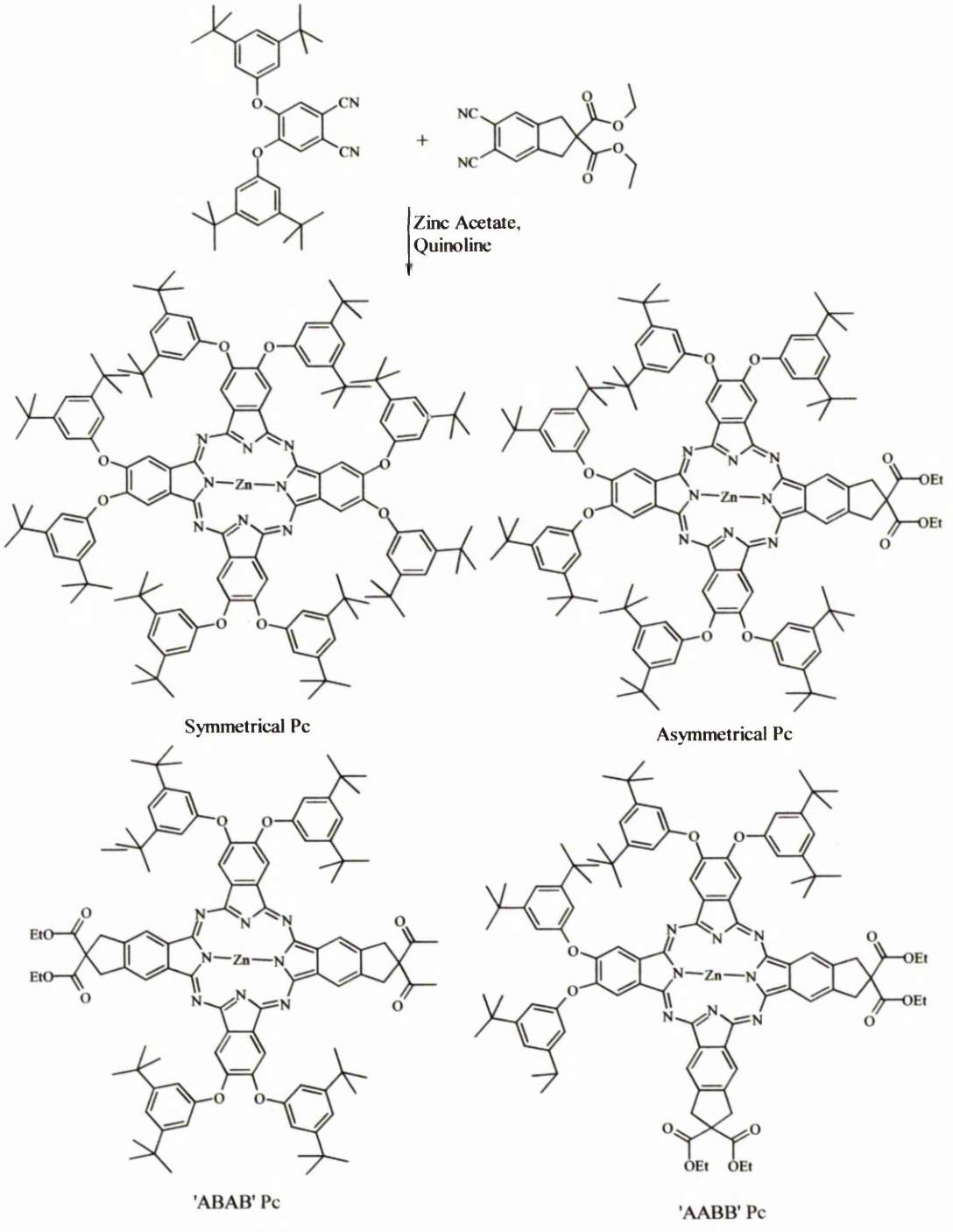


Figure 67: Synthesis of asymmetric Pc with 1,3-diethyl ester functionality

The four products generated were successfully separated using flash column chromatography (eluent: 10:1 40/60 petrol:EtOH). Having isolated the Pc containing a

single 1,3-diethyl ester moiety (the asymmetric Pc, **28,** with each product Pc identified by MALDI mass spectrometry), the barbiturate was introduced(**29**).

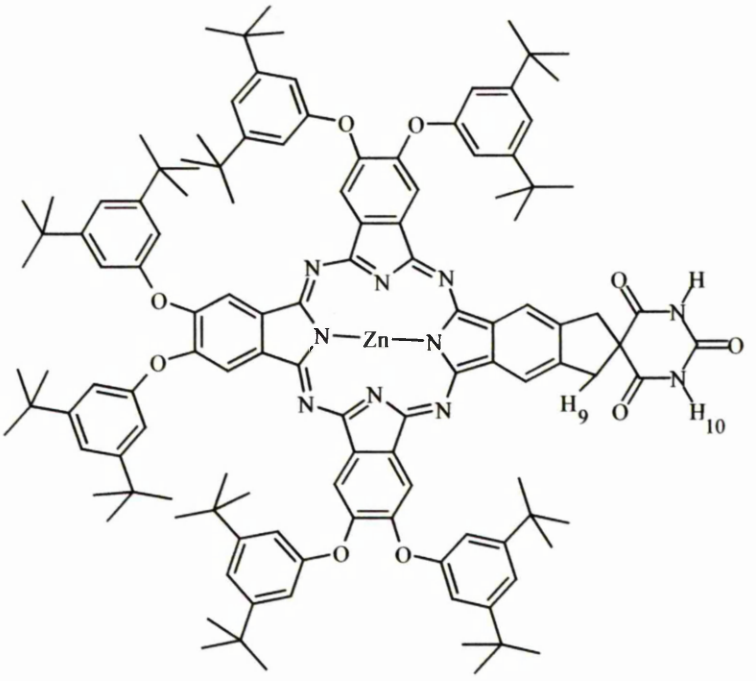


Figure 68: Asymmetric Pc with barbiturate functionality

This was achieved in a similar manner to the formation of the model barbiturate. The product was then mixed with TAP in an attempt to observe the effects of hydrogen bonding. Spectroscopic analysis by proton NMR of the Pc – TAP mixture was performed, with deuterated pyridine as solvent.

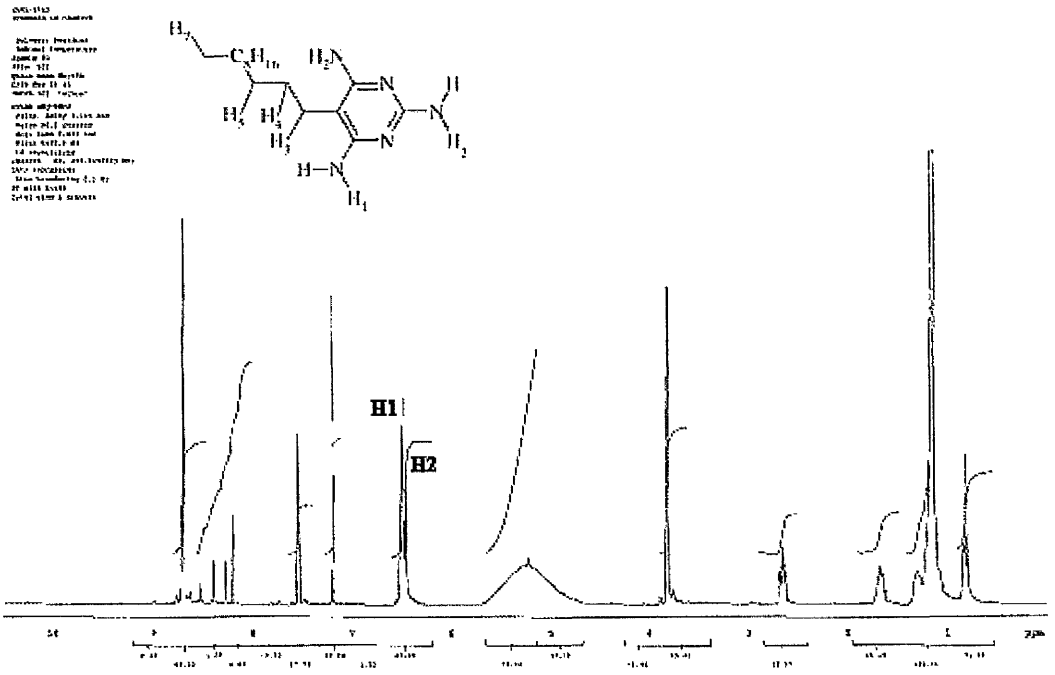


Figure 69: ^{1}H NMR of TAP and Pc barbiturate derivative

The proton NMR showed the functional groups of the two structural components of the gel: the mixed TAP and Pc barbiturate (Figure 69). Also illustrated is the same shift of the TAP NH protons (H1, H2) as that seen the model gel, indicating the formation of hydrogen bonds between the two materials. The precise structure of the pseudo-polymer could not be determined, though this preliminary result indicates the predicted 'ladder' structure to be a possibility.

3.4: References:

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4.0: Conclusions and Further Work

4.1: Synthesis of Indane Based Pcs with Alkyl and Aryl Side Chain Substituents

4.1.1: Conclusions

The synthesis of a homologous series of octa-alkylated Pcs based on the indane ring system was achieved for the alkyl chain lengths hexyl – dodecyl. The materials exhibited a Soret band in the UV region of the electromagnetic spectrum, thus generating the desired cyan colour. However, the level of non- (π) bonding intermolecular interactions were such that all of the Pcs synthesised exhibited thermotropic mesophases. This unexpected property may affect the suitability of the materials as colorants in ink jet inks.

Synthesis of a Pc with aryl species pendant to the Pc core was not achieved. The methodology developed in the synthesis of the alkylated Pc precursors proved unsuccessful when applied to the equivalent aryl molecule.

4.1.2: Further Work

The methodology employed in the synthesis of the octa alkylated Pcs requires further modification to optimise yields. Further characterisation of the Pc mesophases observed in each of the homologous series of Pcs is also required. Precise identification of the transition temperature from crystal to mesophase, and the presence of any mesophase – mesophase transitions should be investigated, as should the measurement of transition temperatures by DSC.

The series of Pcs synthesised were unmetallated. The synthesis of similar metallated species could readily be achieved, leading to an investigation of materials properties. Development of methodology to enable the key reduction of the aryl substituted indanone to the equivalent indane to succeed could be achieved. Successful formation of the indane

would facilitate the possibility of further functionalisation, leading to the formation of indane based Pcs with aryl species pendant to the core Pc.

4.2: Synthesis of Indane Based Pcs with Ester and Amide Side Chain Substituents and 'Ketal' Type Analogues of Indane Esters

4.2.1: Conclusions

Similar indane based octa-carboxylated Pcs, with both zinc and copper as the core metal were synthesised. The possibility of further functionalisation of the carboxyl species pendant to the Pc core was demonstrated by the formation of both the octa carboxylic acid and the octa amide.

Synthesis of the 'ketal' type analogues proved problematic and indicated that these species are probably unsuited to the reaction conditions required for formation of phthalocyanines via traditional methodology.

4.2.2: Further Work

The synthesis of more examples of further functionalised indane based carboxylated Pcs could be attempted. Utilisation of the diethyl ester moiety to generate a variety of esters and amides would be possible, using the methodology demonstrated.

Further review of the possible methods of facilitating Pc formation would be required to attempt the synthesis of the Pc 'ketal' analogues.

4.3: Hydrogen Bonded Supramolecular Systems

4.3.1: Conclusions

Unfortunately, investigations were at a preliminary stage by the end of the time allocated to the project. However, these initial results were encouraging. The synthesis of a model indane containing barbiturate functionality was successfully achieved, and a mixture of the model compound and 5-dodecyl-2,4,6-triaminopyrimidine (TAP) was seen to form a gel in chloroform. Analysis of the mixture by ^{1}H NMR indicated the shift in the N-H peaks resulting from the formation of hydrogen bonds.

The approach was then extended to the synthesis of a Pc containing a barbiturate moiety. The synthesis and isolation of an appropriate asymmetrically substituted Pc containing the prerequisite barbiturate moiety was achieved.

An initial study of a mixture of the Pc-barbiturate and TAP indicated the same shift in N-H peaks previously observed in the model Pc – TAP mixture.

4.3.2: Further Work

Further development of the methodology utilised in the synthesis of the asymmetric Pc is required to improve yields. Characterisation of the intermolecular interactions of the Pc – TAP mixture should be expanded. This would deepen the understanding of the structure of the molecular assembly. The potential study of the mixture by X-ray crystallography and Scanning Electron Microscopy (SEM) should be investigated, and the possibility of the formation of a pseudo – polymeric 'ladder' pursued.

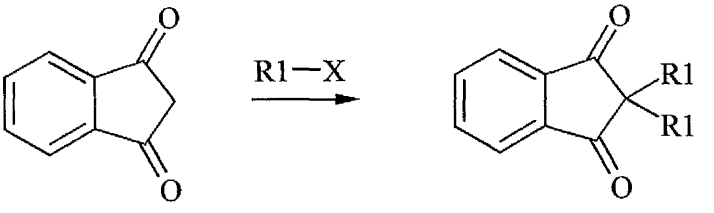
5.0: Experimental

5.1: Reagents and Equipment:

All chemicals were purchased from Aldrich. Solvents were obtained from BDH, and used without purification unless otherwise stated. TLC analysis was performed on Polygram SIL G/UV_{254} 0.25 mm plates. Column chromatography utilised Merck Silica Gel 60 (230-400 mesh). Elemental analyses were obtained using a Carlo Erba Instruments CHNS-O EA 108 Elemental analyser. ^1H NMR spectra were obtained on a Varian Gemini 300 MHz spectrometer. EI/CI mass spectra were acquired on a Fisons Instruments Trio 2000 machine, and MALDI – TOF mass spectra using a Perkin-Elmer Biosystems Voyager. IR spectra were run on a Perkin-Elmer 1710 Fourier Transfer spectrophotometer, and UV/VIS spectra on a Hewlett Packard 8452A Diode Array instrument. Melting points were obtained using a Gallencamp hotstage melting point apparatus and are uncorrected. Optical Microscopy observations were made using a Nikon Optiphot-2 microscope with a Mettler FP80 HT Hot Stage, with the sample between two slides.

5.2: Synthesis of Indane Based Pcs with Alkyl and Aryl Side Chain Substituents

5.2.1: 2,2-Didodecyl-1,3-indanedione 2



A: R1 = $C_{12}H_{25}$, K_2CO_3 (anhydrous), DMF, X = Br, I

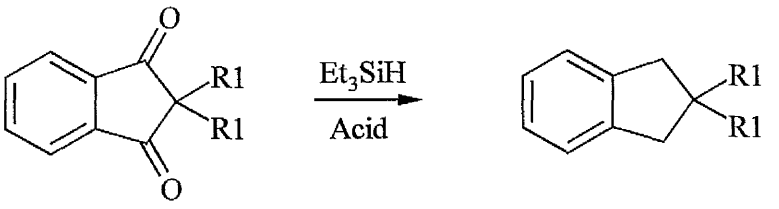
K_2CO_3 (5.67 g) was suspended in DMF (150 ml) with stirring under N_2. The dodecyl iodide (three equivalents, 10 ml, 41.05 mmol) was added via syringe, and the reaction heated to 80° C. The substrate 1,3-indandione **1** (2 g, 13.7 mmol, in 30 ml DMF) was added drop wise over two and a half hours, and the reaction left to stir overnight. The reaction was followed by TLC (eluent 1:1 Et_2O : petrol). When absence of **1** was observed, the reaction mixture was allowed to warm to room temperature. The mixture was then extracted into diethyl ether (250 ml) and washed with water (5 x 500 ml). The organic phase was then dried ($MgSO_4$), filtered and concentrated under reduced pressure to give the crude product. This was then recrystallised (ethanol) to give **2** as yellow crystals (1.6 g, 22 %).

The reaction was repeated using the dodecyl bromide (15 ml, 61.58 mmol). This gave the same product (2.26 g, 22.8 %), *m/z* (CI) 500 (M^+ +H + NH_4^+), 483 (M^+ + H); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.85(t, 6H, 2x $C_{11}H_{22}C\underline{H}_3$), 1.25(m, 40H, 2x $C_{10}\underline{H}_{20}$), 1.9 (m, 4H, 2x $C\underline{H}_2C_{11}H_{23}$), 7.89 (m, 2H, arom), 8.1 (m, 2H, arom).

B: KOH, toluene, DMSO, X = Br, R1 = $C_{12}H_{25}$[2]

KOH (5 g) was suspended in a mixture of toluene and DMSO (1:1, 100 ml in total). 1-bromododecane (three equivalents, 20 ml) was added by syringe. The 1,3-indandione **1** (4 g) was dissolved in toluene and DMSO (1:1 60 ml in total) and added drop wise over one and a half hours. The mixture was allowed to stir under N_2 for two days. The mixture was concentrated under reduced pressure, and extracted into diethyl ether (100 ml). The organic phase was then washed with water (5 x 250 ml), dried ($MgSO_4$), filtered and concentrated in vacuo to give the product **2**, which was then recrystallised from ethanol as above. Yield: 2.26g, 17 %, spectroscopic data as above.

5.2.2: Attempted formation of 2,2-didodecyl indane 3



A: Reduction of 2,2-didodecyl-1,3-indandione with TFA, Et_3SiH, DCM[4]

The diketone **2** (1.28 g) was dissolved in DCM (20 ml) and cooled to 0°C under N_2 with stirring. TFA (six equivalents, 1.82 g) in DCM (10 ml) was added. A solution of triethylsilane (six equivalents, 1.85 g) in DCM (10 ml) was then added drop wise, maintaining the temperature between 0 and 5°C. The reaction mixture was then allowed to warm to room temperature and then refluxed overnight.

The reaction was followed by TLC (eluent – 3:1 petrol:diethyl ether) and MS (EI/CI). With only slight evidence of reaction after two days, the reaction was discontinued in favour of a more concentrated mixture.

B: Reduction of 2,2-didodecyl-1,3-indandione with TFA (as solvent), Et_3SiH[4]

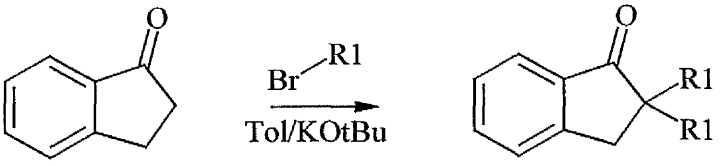
The diketone **2** (1.5 g) was dissolved in TFA (eight equivalents, 2 ml) and triethylsilane (four equivalents, 2 ml) with stirring under N_2. The reaction mixture was then heated to 60°C. After twenty-four hours, TFA (four equivalents, 1 ml) and triethylsilane (two equivalents, 1 ml) were added and the reaction left at 85°C overnight. The process was then repeated over two more days. The reaction was quenched with base ($NaHCO_3$, saturated solution), and extracted with DCM (20 ml). The organic phase was washed with

water (4 x 50 ml), separated, dried ($MgSO_4$), filtered and concentrated to give an oily white solid. The product was purified via column chromatography (eluent – hexane). Bulb to bulb distillation was utilised to remove excess silanes, and the residue gave 0.9 g of a colourless oil. NMR (^1H, 300 MHz) showed a mixture of starting material **2**, product **3** and various silanes.

C: Reduction of 2,2-didodecyl-1,3-indanedione with Et_3SiH, triflic acid, (CF_3SO_3H)[5]

The dione **2** was dissolved in anhydrous DCM (20 ml) and chilled to 0°C under N_2. Triflic acid (four equivalents, 0.75 ml) in anhydrous DCM (15 ml) was added drop wise at 0-5°C. The mixture was stirred under these conditions for one hour. Triethylsilane (three equivalents, 1 ml) in anhydrous DCM (25 ml) was then added drop wise to the mixture and stirred for thirty minutes at 0-5°C. At the end of this period, a further four equivalents of the acid (0.75 ml) in DCM (10 ml) was added drop wise and stirred for a further thirty minutes. A second amount of the silane (1 ml) was added and the reaction vessel allowed to warm to room temperature. After two hours, triethylsilane (1 ml) was added and the reaction stirred under N_2 for forty-eight hours. The reaction was quenched into cold $NaHCO_3$ (saturated soln. 250 ml) and extracted with DCM (3 x 20 ml). The combined organics were dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give a colourless oil. Excess silanes were removed utilising bulb to bulb distillation, giving a green oil as the residue. This was purified using column chromatography (eluent – hexane). The fast running spot was collected and solvent removed to give the product **3** as a colourless oil (0.33g, 33 %), *m/z* (EI) 454 ($M^+ + H$); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.9$ (t, 6H, 2x $C_{11}H_{22}C\underline{H}_3$), 1.3 (bb, 40H, 2x $C_{10}\underline{H}_{20}$), 1.4 (m, 4H, 2x $C\underline{H}_2C_{11}H_{23}$), 2.75 (s, 4H, benzyl), 7.15 (m, 4H, arom.).

5.2.3: 2,2-didodecyl-1-indanone[3] 7a



General procedure; dodecyl bromide:

The alkyl bromide (2.5 equivalents, 27.2 ml, 113.5 mmol) was dissolved in toluene (50 ml, dried on rotary evaporator) and anhydrous potassium tertiary butoxide (KOtBu, 2.5 equivalents, 12 g, 113.5 mmol) suspended in the mixture. 1-indanone **9** (one equivalent, 5g, 37.8 mmol) in toluene (25 ml) was added drop wise over thirty minutes. The reaction mixture was allowed to stir under N_2 for one hour, and a purple suspension formed. The mixture was then heated (three to four hours) at 80°C, and the progress of the reaction followed by TLC (eluent – 2:1 petrol:diethyl ether). The mixture was seen to turn a blue – green colour.

On completion of the reaction, the mixture was allowed to cool to room temperature and quenched into HCl (1M, 200 ml) with stirring (thirty minutes). The organic phase was separated. The lower aqueous phase was extracted with diethyl ether (5 x 25 ml). The combined organic phases were dried ($MgSO_4$), filtered and concentrated under reduced pressure to give the crude dialkylated product as an orange oil. Column chromatography (eluent 2:1 petrol:diethyl ether) and the residue from vacuum distillation yielded the product as an oil (5.31 g, 30 %). *m/z* (CI) 486 ($M^+ + H + NH_4^+$), 468 ($M^+ + H$); ^1H NMR (300 MHz, $CDCL_3$): $\delta = 0.9$ (t, 6H, 2x $C_{11}H_{22}C\underline{H}_3$), 1.3 (m, 40H, $CH_2C_{10}\underline{H}_{20}CH_3$), 1.65 (m, 4H, 2x $C\underline{H}_2C_{11}H_{23}$), 3.03 (s, 2H, benzyl), 7.40 (t, 1H), 7.47 (d, 1H), 7.62 (t, 1H), 7.76 (d, 1H).

The following homologous series of 1-indanone derivatives was prepared using the same conditions:

A: 2,2-diundecyl-1-indanone 7b, Yield: 91 %

m/z (CI) 458 ($M^+ + H + NH_4$), 440 ($M^+ + H$); ^1H NMR (300 MHz, $CDCL_3$): $\delta = 0.9$ (t, 6H, 2x $C_{10}H_{20}C\underline{H}_3$), 1.3 (m, 36H, $CH_2C_9\underline{H}_{18}CH_3$), 1.65 (m, 4H, 2x $C\underline{H}_2C_{10}H_{21}$), 3.03 (s, 2H, benzyl), 7.40 (t, 1H), 7.47 (d, 1H), 7.62 (t, 1H), 7.76 (d, 1H).

B: 2,2-didecyl-1-indanone 7c, Yield: 80 %

m/z (CI) 430 ($M^+ + H + NH_4^+$), 412 ($M^+ + H$); ^1H NMR (300 MHz, $CDCL_3$): $\delta = 0.9$ (t, 6H, 2x $C_9H_{18}C\underline{H}_3$), 1.3 (m, 32H, $CH_2C_8\underline{H}_{16}CH_3$), 1.65 (m, 4H, 2x $C\underline{H}_2C_9H_{19}$), 3.03 (s, 2H, benzyl), 7.40 (t, m 1H), 7.47 (d, 1H), 7.62 (t, 1H), 7.76 (d, 1H).

C: 2,2-dinonyl-1-indanone 7d, Yield: 91 %

m/z (CI) 402 ($M^+ + H + NH_4^+$), 384 ($M^+ + H$); ^1H NMR (300 MHz, $CDCL_3$): $\delta = 0.9$ (t, 6H, 2x $C_8H_{16}C\underline{H}_3$), 1.3 (m, 28H, $CH_2C_7\underline{H}_{14}CH_3$), 1.65 (m, 4H, 2x $C\underline{H}_2C_8H_{17}$), 3.03 (s, 2H, benzyl), 7.40 (t, 1H), 7.47 (d, 1H), 7.62 (t, 1H), 7.76(d, 1H).

D: 2,2-diheptyl-1-indanone 7e, Yield: 92 %

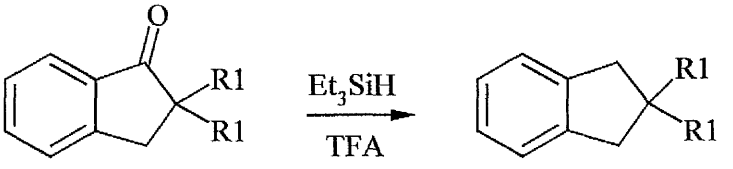
m/z (CI) 346, ($M^+ + H + NH_4^+$), 328 ($M^+ + H$); ^1H NMR (300 MHz, $CDCL_3$): $\delta = 0.9$ (t, 6H, 2x $C_6H_{13}C\underline{H}_3$), 1.3 (m, 20H, 2x $CH_2C_5\underline{H}_{10}CH_3$), 1.65 (m, 4H, 2x $C\underline{H}_2C_6H_{13}$), 3.03 (s, 2H, benzyl), 7.40 (t, 1H), 7.47 (d, 1H,), 7.62 (t, 1H), 7.76 (d, 1H).

E: 2,2-dihexyl-1-indanone 7f, Yield: 91 %

m/z (CI) 318 (M^+ +H + NH_4^+), 300 (M^+ + H); ^{1}H NMR (300 MHz, $CDCL_3$): δ = 0.9 (t, 6H, 2x $C_5H_{11}C\underline{H}_3$), 1.3 (m, 16H, 2x $CH_2C_4\underline{H}_8CH_3$), 1.65 (m, 4H, 2x $C\underline{H}_2C_5H_{11}$), 3.03 (s, 2H, benzyl), 7.40 (t, 1H), 7.47 (d, 1H), 7.62 (t, 1H), 7.76 (d, 1H).

5.2.4: 2,2-didodecyl indane 3a

Ionic hydrogenation; TFA, triethylsilane[4]:



The ketone 2,2-didodecyl 1-indanone (7.92 g)was dissolved in TFA (4 equivalents, 30 ml) and triethylsilane (2 equivalents, 5.2 ml). The reaction mixture was heated to 80°C and the reaction followed by TLC (eluent – hexane + 10% DCM), MS (EI/CI), and ^{1}H NMR (300MHz, $CDCl_3$). Further triethylsilane (2 equivalents per day) was added over 3 days, until no more starting material could be seen. On completion of the reaction, the mixture was quenched into $NaHCO_3$ (saturated soln.) and extracted with DCM. The separated organic phase was dried ($MgSO_4$) filtered and concentrated *in vacuo* to give the crude product. Silane residues were removed utilising bulb to bulb distillation, and trace starting materials via column chromatography (eluent - hexane) to give the product as a colourless oil (4.49 g, 61 %). *m /z* (EI) 454 (M^+ + H); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.9 (t, 6H, 2x $C_{11}H_{22}C\underline{H}_3$), 1.3(m, 40H, 2x $C_{10}\underline{H}_{20}$), 1.4 (m, 4H, 2x $C\underline{H}_2C_{11}H_{23}$), 2.75 (s, 4H, benzyl), 7.15 (m, 4H, arom.).

The process was repeated for several substrates using this method :

B: 2,2-didecyl indane 3c Yield: 55 %

m/z (EI) 398 ($M^+ + H$); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.9$ (t, 6H, 2x $C_9H_{18}C\underline{H}_3$), 1.3 (m, 32H, 2x $C_8\underline{H}_{16}$), 1.4 (m, 4H, 2x $C\underline{H}_2C_9H_{18}$), 2.75 (s, 4H, benzyl), 7.15 (m, 4H).

C: 2,2-dinonyl indane 3d Yield: 56 %

m/z (EI) 370 ($M^+ + H$); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.9$ (t, 6H, 2x $C_8H_{16}C\underline{H}_3$), 1.3 (m, 28H, 2x $C_7\underline{H}_{14}$), 1.4 (m, 4H, 2x $C\underline{H}_2C_8H_{17}$), 2.75 (s, 4H, benzyl), 7.15 (m, 4H,).

D: 2,2-diheptyl indane 3e Yield: 28 %*

m/z (EI) 314 ($M^+ + H$); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.9$ (t, 6H, 2x $C_6H_{12}C\underline{H}_3$), 1.3 (m, 20H, 2x $C_5\underline{H}_{10}$), 1.4 (m, 4H, 2x $C\underline{H}_2C_6H_{13}$), 2.75 (s, 4H, benzyl), 7.15 (m, 4H).

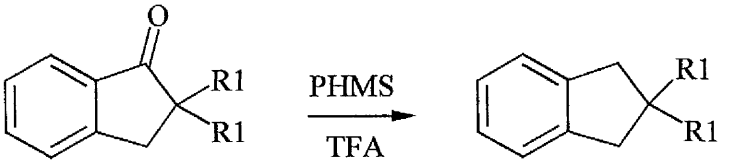
*$BF_3.Et_2O$ (cat.) used to attempt to speed up reaction

E: 2,2-dihexyl indane 3f Yield: 56 %

m/z (EI) 286 ($M^+ + H$); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.9$ (t, 6H, 2x $C_5H_{10}C\underline{H}_3$), 1.3 (m, 16H, 2x $C_4\underline{H}_8$), 1.4 (m, 4H, 2x $C\underline{H}_2C_5H_{11}$), 2.75 (s, 4H, benzyl), 7.15 (m, 4H).

5.2.5: 2,2-diundecyl indane 3b

i) Ionic hydrogenation; TFA, Poly(hydromethylsiloxane) (PHMS)



The ketone 2,2-diundecyl 1-indanone was dissolved in TFA (50 ml) and stirred for 30 minutes under nitrogen. This was followed by addition of poly(hydromethylsiloxane) (PHMS) (10 g, 22mmol.) The reaction was heated to 80°C and $BF_3.Et_2O$ (catalytic) added via pipette. The mixture was maintained under these conditions for three days.

The reaction mixture was taken up in DCM and quenched into NaOH (10% w/w). The resultant organic suspension was separated and filtered through a silica plug. The liquors were then concentrated to give the product as a colourless oil (g, 36 %). *m/z* (EI) 426 ($M^+ + H$); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.9$ (t, 6H, 2x $C_{10}H_{20}C\underline{H}_3$), 1.3 (m, 36H, 2x $C_9\underline{H}_{18}$), 1.4 (m, 4H, 2x $C\underline{H}_2C_{10}H_{21}$), 2.75 (s, 4H, benzyl), 7.15 (m, 4H).

Several other indanes were prepared via this method:

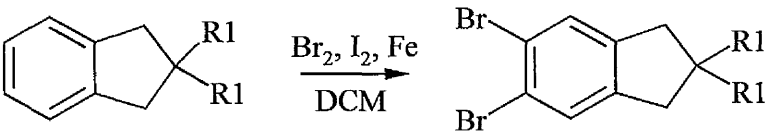
Substrate R1	Mmols. PHMS used	Yield %
3d C_9H_{19}	20.6	28
3e C_7H_{15}	22.2	30
3f C_6H_{13}	3.3	58*

*Impure – large amount of poly siloxanes present.

ii) Catalytic hydrogenation; Hydrogen, palladium/charcoal

The ketone 2,2-diundecyl 1-indanone (**7b**)(3.76 g, 8.5 mmol.0 was dissolved in ethanol (150 ml) and palladium (10 %, on activated charcoal, catalytic) added. The reaction mixture was placed with vigorous stirring under a hydrogen atmosphere. The reaction was followed by T.L.C. (eluent – hexane + 10 % DCM) and was completed after four days. The reaction mixture was then filtered to remove catalyst, solvent removed under reduced pressure and the residue purified via column chromatography (eluent – hexane) to give the product (**3b**) as a colourless oil (2.84 g, 76 %). Characterisation as before.

5.2.6: 3,4-dibromo-8,8-didodecyl indane 4a



$R1 = C_{12}H_{25}, C_{10}H_{21}, C_9H_{19}, C_7H_{15}, C_6H_{13}$

General procedure; 8-didodecyl indane:

The indane **3a** (4.49 g, 9.88 mmol) was dissolved in DCM (20 ml) and cooled on ice. Iron granules and iodine (catalytic) were added. Bromine (2 equivalents, 1.14 ml, 19.78 mmol) in DCM (30 ml) was added drop wise over one hour. On completion of the addition the reaction mixture was allowed to warm to room temperature and stir under nitrogen for two hours. The reaction was followed by TLC (eluent – 1:1 DCM:hexane). When the TLC showed no starting material, the mixture was quenched into sodium bisulfite solution (saturated). The organics were extracted with DCM, dried ($MgSO_4$), filtered and concentrated under reduced pressure to give the dibromide **4a** (5.02 g, 83 %). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.94 (6H, t, $C_{11}H_{22}C\underline{H}_3$), 1.29 (40H, b, $CH_2C_{10}\underline{H}_{20}CH_3$), 1.42 (4H, m, 2x $C\underline{H}_2C_{11}H_{23}$), 2.7 (4H, s, benzyl), 7.4 (2H, s); *m/z* (EI) 612 ($M^+ + H$).

The process was repeated for five other substrates:

Characterisation:

A: 3,4-dibromo-8,8-diundecyl indane 4b Yield: 67 %

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.94 (t, 6H, 2x $C_{10}H_{20}C\underline{H}_3$), 1.29 (b, 32H, 2x $CH_2C_9\underline{H}_{18}CH_3$), 1.42 (m, 4H, 2x $C\underline{H}_2C_{10}H_{21}$), 2.7 (s, 4H, benzyl), 7.4 (s, 2H); *m/z* (EI) 584 ($M^+ + H$).

B: 3,4-dibromo-8,8-didecyl indane 4c Yield: 80 %

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.94 (t, 6H, 2x $C_9H_{18}C\underline{H}_3$), 1.29 (b, 32H, 2x $CH_2C_8\underline{H}_{16}CH_3$), 1.42 (m, 4H, 2x $C\underline{H}_2C_9H_{19}$), 2.7 (s, 4H, benzyl), 7.4 (s, 2H); *m/z* (EI) 556 ($M^+ + H$).

C: 3,4-dibromo-8,8-dinonyl indane 4d Yield: 84 %

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.94 (t, 6H, 2x $C_8H_{16}C\underline{H}_3$), 1.29 (b, 28H, 2x $CH_2C_7\underline{H}_{14}CH_3$), 1.42 (m, 4H, 2x $C\underline{H}_2C_8H_{17}$), 2.7 (s, 4H, benzyl), 7.4(s, 2H); *m/z* (EI) 528 ($M^+ + H$).

D: 3,4-dibromo-8,8-diheptyl indane 4e Yield: 83 %

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.94 (t, 6H, 2x $C_6H_{12}C\underline{H}_3$), 1.29 (b, 20H, 2x $CH_2C_5\underline{H}_{10}CH_3$), 1.42 (m, 4H, 2x $C\underline{H}_2C_6H_{13}$), 2.7 (s, 4H, benzyl), 7.4 (s, 2H); *m/z* (EI) 472 ($M^+ + H$).

E: 3,4-dibromo-8,8-dihexyl indane 4f Yield: 84 %

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.94 (t, 6H, 2x $C_5H_{10}C\underline{H}_3$), 1.29 (b, 16H, 2x $CH_2C_4\underline{H}_8CH_3$), 1.42 (m, 4H, 2x $C\underline{H}_2C_5H_{11}$), 2.7 (s, 4H, benzyl), 7.4 (s, 2H); *m/z* (EI) 444 ($M^+ + H$).

5.2.7: 3,4-dicyano-8,8-didodecyl indane 5a

R1 = $C_{12}H_{25}$, $C_{11}H_{23}$, $C_{10}H_{21}$, C_9H_{19}, C_7H_{15}, C_6H_{13}

The dibromide **4a** (5.02 g, 8.2 mmol) was taken up in DMF (large excess, approx 150ml) via syringe transfer. Copper cyanide (four equivalents, 2.9 g, 32.81 mmol) was added and the reaction heated to 160° C under N_2 for six hours, then left at 120°C overnight. The temperature was then raised (160°C, six hours) and a further two equivalents of CuCN added. The reaction was followed by TLC (eluent 1:1 DCM:hexane). When no more starting material was present, the reaction was allowed to cool to room temperature. The reaction mixture was poured into ammonia solution (35%) to quench excess CuCN, and

the organics were extracted with DCM. The organic phase was washed with NH_3 until the upper aqueous phase was no longer blue, then with water to remove traces of DMF. The solution was dried, filtered and solvent removed to give the crude phthalonitriles. Purification was achieved via column chromatography (eluent – 1:1 DCM:hexane), and the product **5a** isolated (0.76 g, 18 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.92 (t, 6H, 2x $C_{11}H_{22}C\underline{H}_3$), 1.3 (m, 40H, 2x $CH_2C_{10}\underline{H}_{20}CH_3$), 1.44 (m, 4H, 2x $C\underline{H}_2C_{11}H_{23}$), 2.87 (s, 4H, benzyl), 7.6 (s, 2H); *m/z* (EI) 504 ($M^+ + H$).

The following materials were prepared using similar methodology:

B: 3,4-dicyano-8,8-diundecyl indane 5b Yield: 25 %

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.92 (t, 6H, 2x $C_9H_{18}C\underline{H}_3$), 1.3 (m, 32H, 2x $CH_2C_9\underline{H}_{18}CH_3$), 1.44 (m, 4H, 2x $C\underline{H}_2C_{10}H_{21}$), 2.87 (s, 4H, benzyl), 7.6 (s, 2H); *m/z* (EI) 476 ($M^+ + H$).

C: 3,4-dicyano-8,8-didecyl indane 5c Yield: 35 %

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.92 (t, 6H, 2x $C_8H_{16}C\underline{H}_3$), 1.3 (m, 32H, 2x $CH_2C_8\underline{H}_{16}CH_3$), 1.44 (m, 4H, 2x $C\underline{H}_2C_9H_{19}$), 2.87 (s, 4H, benzyl), 7.6 (s, 2H); *m/z* (EI) 448 ($M^+ + H$).

D: 3,4-dicyano-8,8-dinonyl indane 5d Yield: 39 %

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.92 (t, 6H, 2x $C_7H_{14}C\underline{H}_3$), 1.3 (m, 28H, 2x $CH_2C_7\underline{H}_{14}CH_3$), 1.44 (m, 4H, 2x $C\underline{H}_2C_8H_{17}$), 2.87 (s, 4H, benzyl), 7.6(s, 2H); *m/z* (EI) 420 ($M^+ + H$).

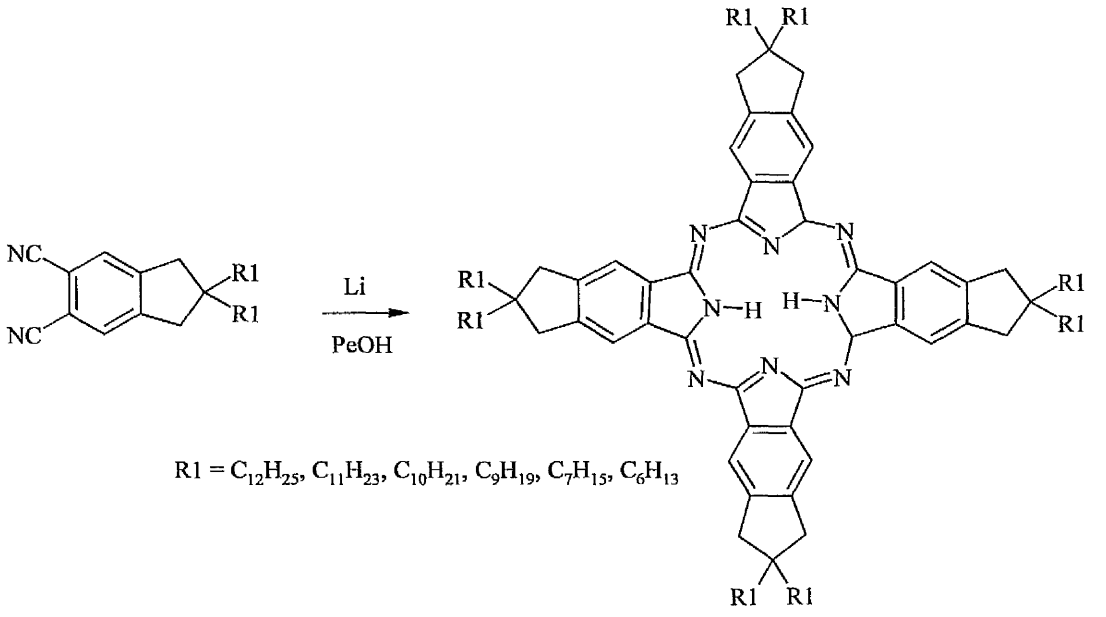
E: 3,4-dicyano-8,8-diheptyl indane 5e Yield: 100 %

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.92 (t, 6H, 2x $C_5H_{10}C\underline{H}_3$), 1.3 (m, 20H, 2x $CH_2C_5\underline{H}_{10}CH_3$), 1.44 (m, 4H, 2x $C\underline{H}_2C_6H_{13}$), 2.87 (s, 4H, benzyl), 7.6 (s, 2H); *m/z* (EI) 364 ($M^+ + H$).

F: 3,4-dicyano-8,8-dihexyl indane 5f Yield: 43 %

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.92 (t, 6H, 2x $C_4H_8C\underline{H}_3$), 1.3 (m, 16H, 2x $CH_2C_4\underline{H}_8CH_3$), 1.44 (m, 4H, 2x $C\underline{H}_2C_5H_{11}$), 2.87 (s, 4H, benzyl), 7.6 (s, 2H); *m/z* (EI) 336 ($M^+ + H$).

5.2.8: Phthalocyanine formation



R1 = $C_{12}H_{25}$, $C_{11}H_{23}$, $C_{10}H_{21}$, C_9H_{19}, C_7H_{15}, C_6H_{13}

Tetra-cyclisation of 3,4-dicyano-8,8-didecyl indane 8c

The phthalonitrile 3,4-dicyano-8,8-didecyl indane **5c** (237 mg, 0.53 mmol) was dissolved in pentan-1-ol (2 ml, dried via azeotrope with toluene) and heated under N_2 to 120°C. On temperature equilibration, Lithium (5.4 equivalents, 20 mg, 2.9 mmol) was added, and the immediate formation of the Pc was observed. The reaction conditions were maintained until no more evidence of the phthalonitrile was seen in the TLC (eluent – 1:1 DCM:hexane approximately three hours). The reaction vessel was then allowed to cool to room temperature and quenched into methanol (50 ml) and acetic acid (1 ppt). The resultant suspension was separated via centrifugation, the methanol/acetic acid decanted and the residue washed by repeated centrifuging until the methanol was colourless. The residue was then extracted and purified by column chromatography (eluent - 1:1 DCM:hexane) to give the final product **8c** (80 mg, 8 %). The product was then characterised. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.93 (t, 24H), 1.0 – 1.6 (b, 128H), 1.75

(m, 16H), 3.3 (s, 16H), 8.6 (s, 8H); λ_{max} (CH_2Cl_2): 660nm, 700nm(sharp); *m/z* (MALDI) 1798 (M^+); (Calc. for $C_{124}H_{194}N_8$: C, 82.88; H, 10.88; N, 6.24. Found: C, 81.99; H, 10.67; N, 7.40 %).

The following materials were synthesised via the same methology:

A: R1: $C_{12}H_{25}$; **8a** Yield: 7 %

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.93 (t, 24H), 1.0 – 1.6 (b, 160H), 1.75(m, 16H,), 3.3 (s, 16H), 8.6 (s, 8H); λ_{max} (CH_2Cl_2): 660nm, 700nm(sharp); *m/z* (MALDI) 2022 (M^+); (Calc. for $C_{140}H_{226}N_8$: C, 83.19; H, 11.27; N, 5.54. Found: C, 83.11; H, 11.90; N, 5.47 %).

B: R1: $C_{11}H_{23}$; **8b** Yield: 4 %

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.93 (t, 24H), 1.0 – 1.6 (m, 144H), 1.75(m, 16H,), 3.3 (s, 16H), 8.6 (s, 8H); λ_{max} (CH_2Cl_2): 660nm, 700nm(sharp); *m/z* (MALDI) 1910 (M^+); (Calc. for $C_{132}H_{210}N_8$: C, 83.04; H, 11.09; N, 5.87. Found: C, 82.14; H, 11.51; N, 5.70 %).

C: R1: C_9H_{19}; **8d** Yield: 3 %

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.93 (t, 24H), 1.0 – 1.6 (b, 112H), 1.75 (m, 16H), 3.3 (s, 16H), 8.6 (s, 8H); λ_{max} (CH_2Cl_2): 660nm, 700nm(sharp); *m/z* (MALDI) 1686 (M^+); (Calc. for $C_{116}H_{178}N_8$: C, 82.70; H, 10.65; N, 6.65. Found: C, 82.44; H, 10.68; N, 6.36 %).

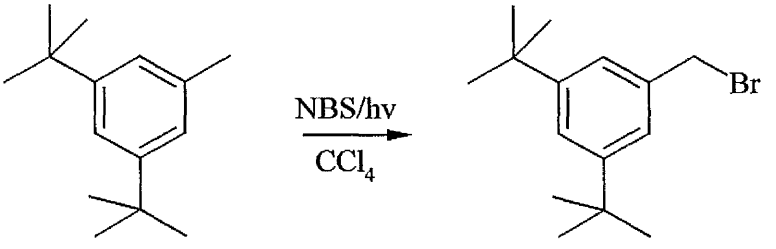
D: R1: C_7H_{15}; **8e** Yield: 4 %

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.93 (t, 24H), 1.0 – 1.6 (b, 80H), 1.75 (m, 16H), 3.3 (s, 16H), 8.6 (s, 8H); λ_{max} (CH_2Cl_2): 660nm, 700nm(sharp); *m/z* (MALDI) 1462 (M^+); (Calc. for $C_{110}H_{146}N_8$: C, 82.25; H, 10.08; N, 7.67. Found: C, 80.93; H, 9.91; N, 7.22 %).

E: R1: C_6H_{13}; **8f** Yield: 4 %

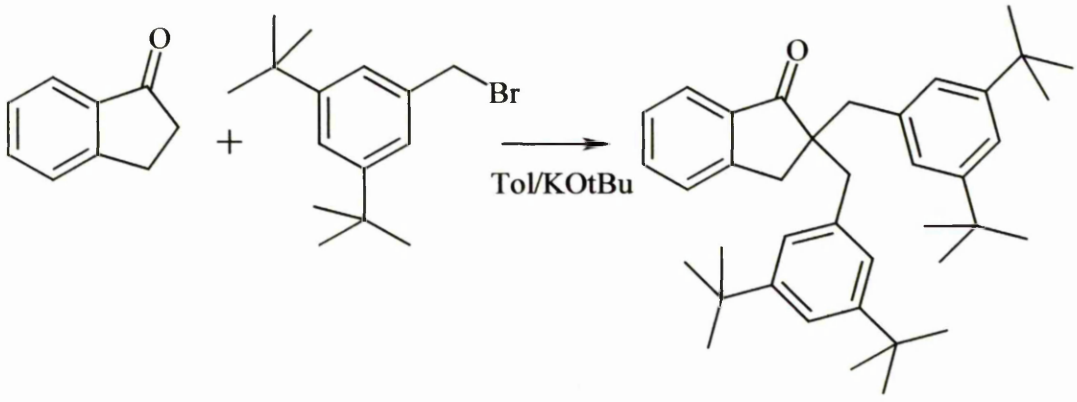
^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.93 (t, 24H), 1.0 – 1.6(b, 64H), 1.75 (m, 16H), 3.3 (s, 16H), 8.6 (s, 8H); λ_{max} (CH_2Cl_2): 660nm, 700nm(sharp); m/z (MALDI) 1350 (M^+); (Calc. for $C_{102}H_{130}N_8$: C, 81.97; H, 9.72; N, 8.31. Found: C, 81.00; H, 9.94; N, 7.71 %).

5.2.9: 1-Bromomethyl-3,5–di-tert-butyl benzene 9



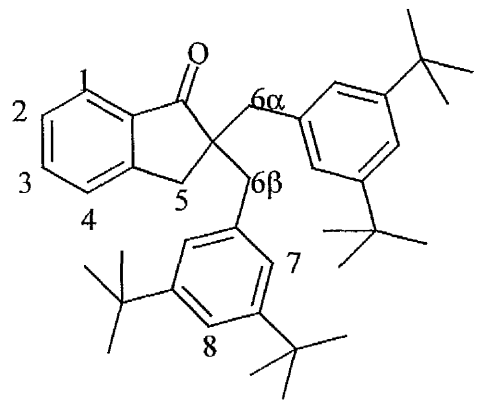
CCl_4 (30 ml) and 3,5-di-tertiary butyl toluene (4 g) were placed with stirring under N_2. NBS (3.49 g) was added and the reaction was then activated with a tungsten lamp. After three hours TLC (eluent – hexane) showed no evidence of starting material and the reaction was stopped. DCM and H_2O were added, the mixture partitioned and the lower organic phase collected. The solvent was then evaporated to give an oil (**9**). (4.72g, 85 %). ^{1}H NMR (300MHz, $CDCl_3$) δ = 1.38 (18H, b, 2x tBu), 4.6 (2H, s, benzyl), 7.29 (2H, s), 7.42 (1H, s).

5.2.10: 2,2-Bis-(3,5-di-tert-butyl-benzyl)-indan-1-one 10



The dibromide **9** (2.5 – 3 equivalents) was dissolved in toluene (50ml, dried on rotary evaporator) and potassium tertiary butoxide (KOtBu, 2.5 – 3 equivalents) suspended in the mixture. 1-indanone **9** (one equivalent) in toluene (25ml, dry) was added drop wise over thirty minutes. The reaction mixture was allowed to stir under N_2 for one hour, and a purple suspension formed. The mixture was then heated (three to four hours) at 80°C,

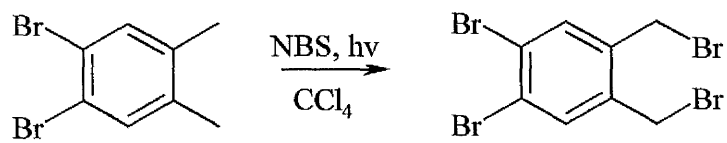
On completion of the reaction, the mixture was allowed to cool to room temperature and quenched into HCl (1M, 200ml) with stirring (thirty minutes). The upper organic phase was separated. The lower aqueous phase was extracted with diethyl ether (5x25ml). The combined organics were dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the product **10** as an oil. (g, 100 %). ^{1}H NMR (300MHz, $CDCL_3$) δ = 1.24(36H, s, 4x tBu), 2.92(2H, d, H6β), 3.06(2H, s, H5), 3.32(2H, d, H6α), 6.96(4H, s, H7), 7.10(1H, t, H3), 7.13(2H,s, H8), 7.15(1H, d, H4), 7.3(1H, t, H2), 7.6(1H,d, H1).



5.3: Indane Based Pcs with Ester and Amide Side Chain Substituents

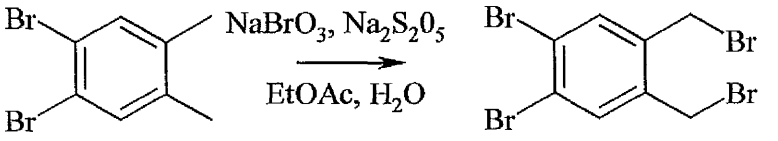
5.3.1: 4,5-Bis(bromomethyl)-1,2-dibromobenzene 13

i) With NBS:



4,5-Dibromo-o-xylene (15g, 56.8mmol) was dissolved in CCl_4 (200ml) and nitrogen bubbled through the solution. N-Bromo-succinimide (20.22g, 113.6mmol) was added and the mixture photolysed overnight under nitrogen. On completion of the reaction the solvent was removed under reduced pressure and the resultant solid extracted in toluene and washed with brine. The toluene solution was dried over magnesium sulfate, filtered and solvent removed under reduced pressure to give the crude material. This was the recrystallised (DCM) to give the product (13.6g, 57 %) mp 124-125 ° C, *m/z* (EI) 422 (M^+), 342 (M^+ - Br); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.58$ (s, 4H), 7.63 (s, 2H).

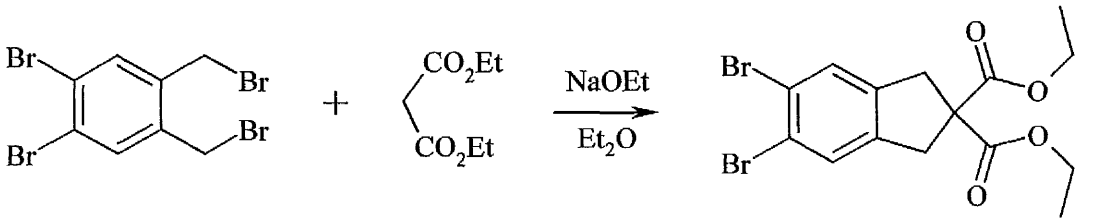
ii) 'Two Phase' bromination:



The dibromide (13g, 51mmol) was dissolved in EtOAc (150ml) and stirred vigorously. Sodium bromate (30.57g, 203.8mmol) as an aqueous solution (150ml water) was then added to the reaction vessel. Sodium metabisulfite solution (19.3g, 101.5mmol) in water (150ml) was added dropwise over two hours. The mixture was allowed to stir overnight. Further portions of $NaBrO_3$ (2 equivalents, 15.29g in 75ml water) and $Na_2S_2O_5$ (one equivalent, 9.65g in 75ml water) were added, and the reaction allowed to stir for a further twenty four hours. NMR indicated incomplete reaction and thus a third portion of each reagent ($NaBrO_3$: 2 equivalents, 15.29g in 75ml water, $Na_2S_2O_5$: one equivalent, 9.65g in 75ml water) was added and the reaction stirred overnight.

The organic phase was then separated and the aqueous phase washed with Et_2O (3x50ml). The combined organics were then quenched with sodium metabisulfite (saturated aqueous solution) until completely decolourised. Separation of organics was followed by drying over magnesium sulfate, filtration, and removal of solvent under reduced pressure to give the crude product. This was recrystallised from DCM to give the purified product as a white solid (15g, 72 %).

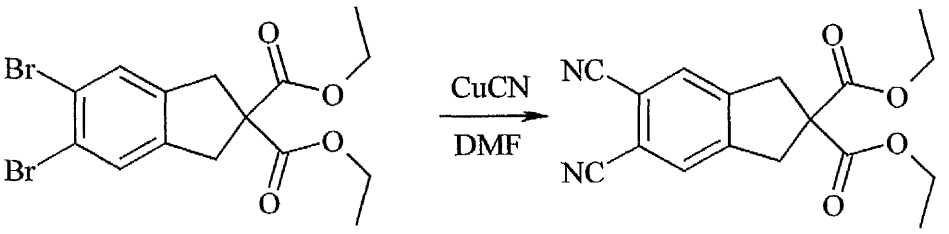
5.3.2: Diethyl 5,6-dibromoindan-2,2-dicarboxylate 14



Sodium ethoxide (2.37g, 34.8mmol), was suspended in anhydrous diethyl ether (100ml) under nitrogen. Diethyl malonate (2.28g, 14.2mmol) was then added by syringe and the mixture stirred for thirty minutes. The tetra bromide 4,5-bis(bromomethyl)-1,2-dibromobenzene (**13**) (6.68g, 15.8mmol) in anhydrous diethyl ether (50ml) was transferred to the reaction vessel via syringe. The reagents were then heated to reflux for five hours. The reaction was followed by T.L.C. (eluent: 5:1 40/60 petrol:EtOAc)

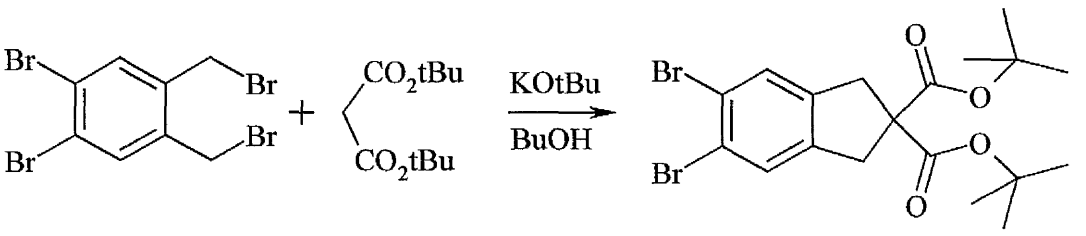
When the reaction was shown to be complete, the vessel was allowed to cool to room temperature, and $HCl_{(aq)}$ (1M, 100ml) was added. The organic phase was separated and the aqueous phase washed with diethyl ether (3x50ml). The combined organics were dried over magnesium sulfate, filtered and solvent removed under reduced pressure to give the crude product as a yellow oil. The crude material was purified by column chromatography (eluent as T.L.C) to give the diester **14** as a white solid (3.35g, 50 %). Mp. 66 – 68 ° C, *m/z* (CI) 438 ($M^+ + NH_4^+$), 421 ($M^+ + H$), 358 ($M^+ - Br + NH4^+$); 1H NMR (300 MHz, CDCl3): δ = 1.3 (t, 6 H), 3.56 (s, 4 H), 4.22 (q, 4 H), 7.48 (s, 2H); (Calc. for $C_{15}H_{16}Br_2O_4$: C, 42.89; H, 3.84; Br, 38.04. Found: C, 41.29; H, 3.49; Br, 38.97 %).

5.3.3: Diethyl 5,6-dicyanoindan-2,2-dicarboxylate 15



Diethyl 5,6-dibromoindan-2,2-dicarboxylate **14** (1g, 2.3mmol) was dissolved in anhydrous DMF (2ml) and CuCN (4.26g, 47.36mmol) added under nitrogen. The reagents were heated to 150°C for six hours, monitored by T.L.C (eluent: DCM). Once the dibromide had fully reacted, as shown by T.L.C. the reaction mixture was allowed to cool to room temperature. Copper residues were removed via addition of ammonia solution. The organics were taken up in DCM, and washed with aqueous ammonia solution until no evidence of colour was seen in the aqueous phase (approx. 10x50ml). The organic phase was filtered to remove insoluble copper salts and purified by gradient column chromatography (eluent: 5:1 toluene:THF – THF). The phthalonitrile was isolated as a white solid (0.67g, 90 %). Mp. 117 - - 119 ° C, *m/z* (CI) 330 ($M^+ + NH4^+$); ^1H NMR (300 MHz, $CDCl_3$): δ = 1.32 (t, 6H), 3.74 (s, 4H), 4.27 (q, 4H), 7.68 (s, 2H); (Calc. for $C_{17}H_{16}N_2O_4$: C, 65.38; H, 5.16; N, 8.97. Found: C, 65.02; H, 5.02; N, 8.89 %).

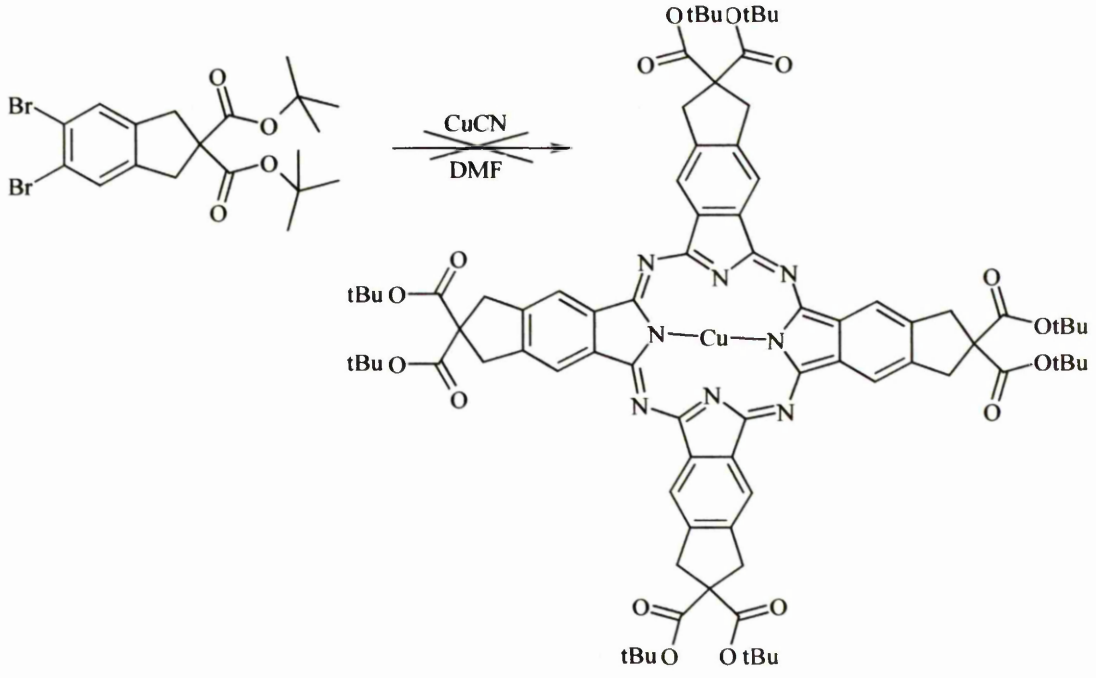
5.3.4: Di-t-butyl 5,6-Dibromoindan-2,2-dicarboxylate 21



Potassium tert-butoxide (1.75g, 15.64mmol), was suspended in tertiary butanol (10ml) under nitrogen. Di-tertiarybutyl malonate (1.96g, 7.82mmol) was then added by syringe and the mixture stirred for thirty minutes. The tetra bromide 4,5-bis(bromomethyl)-1,2-dibromobenzene **13** (3g, 7.11mmol) in anhydrous diethyl ether (50ml) was transferred to the reaction vessel via syringe. The reagents were then heated to reflux for five hours. The reaction was followed by T.L.C. (eluent: 5:1 40/60 petrol:EtOAc)

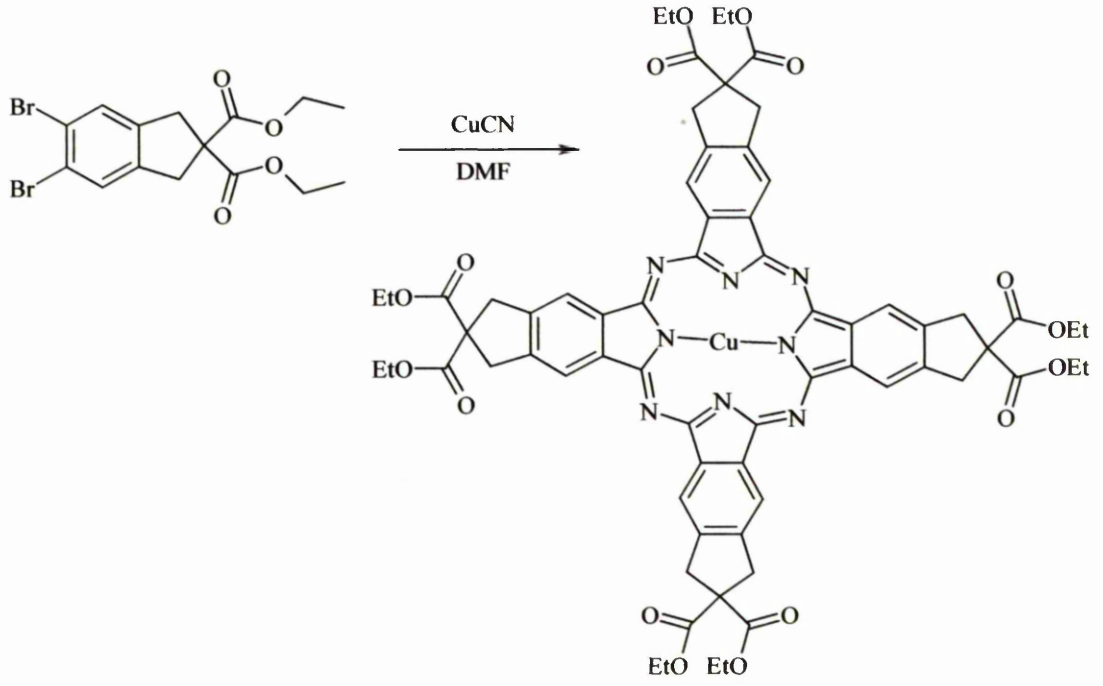
When the reaction was shown to be complete, the vessel was allowed to cool to room temperature, and HCl $_{(aq)}$ (1M, 100ml) was added. The organic phase was separated and the aqueous phase washed with diethyl ether (3x50ml). The combined organics were dried over magnesium sulfate, filtered and solvent removed under reduced pressure to give the crude product as a yellow oil. The crude material was purified by recrystallisation (hexane) to give the diester as a yellow solid (0.51g, 15 %), *m/z* (CI) 494 ($M^+ + H + NH_4^+$) 477 ($M^+ + H$), 438 ($M^+ + H + NH_4^+$ - tButyl), 358 ($M^+ + H + NH4^+$ - tButyl – Br); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.50$ (s, 18H), 3.44 (s, 4H), 7.47 (s, 2H).

5.3.5: Attempted cyclisation of di-t-butyl 5,6-dibromoindan-2,2-dicarboxylate to form phthalocyanine derivative



Di-t-butyl 5,6-dibromoindan-2,2-dicarboxylate (0.51g, 1.07mmol) was dissolved in anhydrous DMF (1ml) with stirring under nitrogen. Copper cyanide (0.96g, 10.6mmol) was added and the reaction vessel heated to 160°C for 48 hours. No evidence of phthalocyanine formation was observed and the reaction was abandoned.

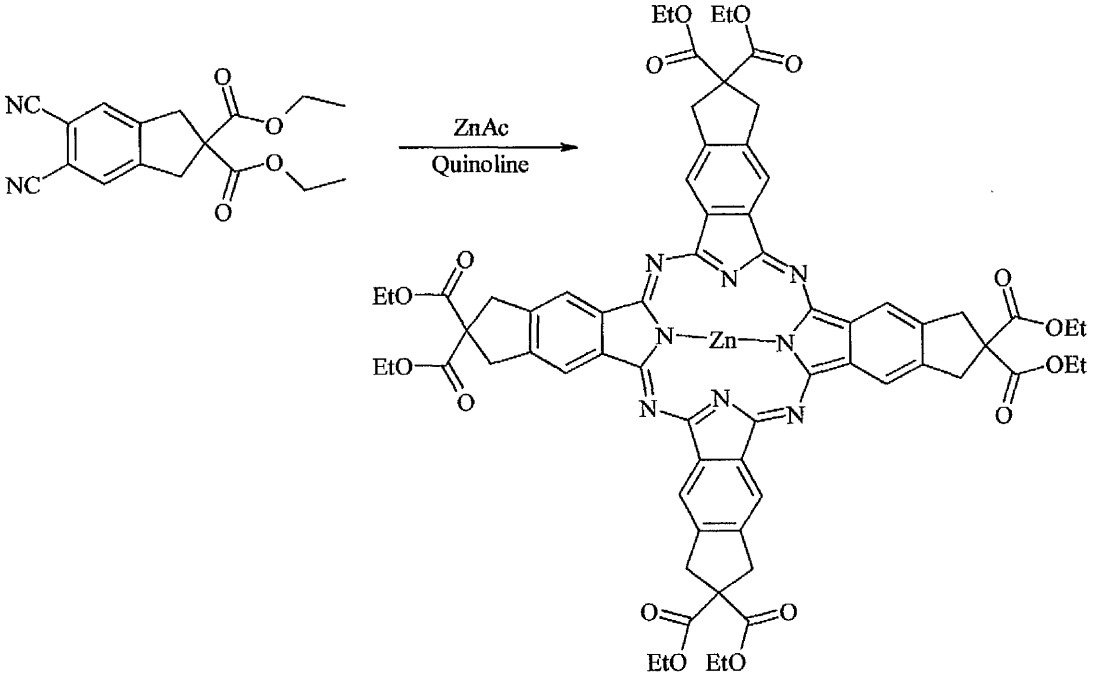
5.3.6: Cyclisation of diethyl 5,6-dibromoindan-2,2-dicarboxylate 14 to form copper phthalocyanine derivative 16.



Copper cyanide (1.06g, 12mmol) was added to a stirred solution of diethyl 5,6-dibromoindan-2,2-dicarboxylate **14** (0.5g, 1.2mmol) in anhydrous DMF (2ml) under nitrogen. The reagents were heated to 180°C for 48 hours, and the characteristic deep blue colour of copper phthalocyanine was seen to develop. The reaction vessel was allowed to cool to room temperature and ammonia solution (33% aqueous, 50ml) added to quench excess copper cyanide residues. The mixture was stirred overnight. Ethyl acetate (20 ml) was added and the organic phase washed with ammonia solution (10x50ml) until no more evidence of the deep blue ammoniacal copper cyanide complex could be seen. The organic phase was then washed with water (3x50ml) and brine (2x50ml), before separation of the upper organic phase, drying over magnesium sulfate, filtration and removal of solvent to generate the crude phthalocyanine. Purification of this material was achieved by gradient column chromatography (eluent: 5:1 toluene:THF – THF), giving the pure product

16 as a blue/black solid (100 mg, 5 %), *m/z* (MALDI) 1313 (M^+); λ_{max} (toluene): 768 nm (sharp single peak); (Calc. for $C_{68}H_{64}N_8O_{16}Cu$: C, 62.21; H, 4.91; N, 8.54. Found: C, 62.46; H, 4.59; N, 8.69 %).

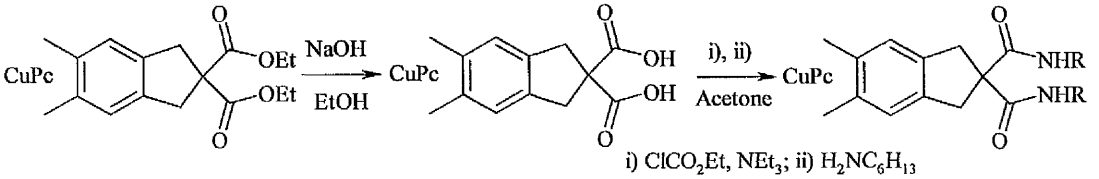
5.3.7: Cyclisation of 5,6-dicyanoindan-2,2-dicarboxylic acid diethyl ester 15 to form zinc phthalocyanine derivative 18.



A solution of the phthalonitrile (0.66g, 1.6mmol) in distilled quinoline (1ml) was stirred under nitrogen. To this was added anhydrous zinc acetate (1.15g, 6.3mmol) and the reagents heated to 180°C for twenty four hours. Formation of the characteristic deep green of zinc phthalocyanine was observed. The mixture was poured into methanol (20ml) and the product precipitated. Separation was achieved via centrifugation followed by filtration and the product was isolated as a deep green solid (140 mg, 7 %). *m/z* (MALDI) 1314

(M^+), ^1H NMR (300 MHz, $CDCl_3$): δ = 1.2 (t, 6H), 3.8 (s,4H), 4.4 (q, 4H), 8.2 (s, 12H), 8.25 (s, 6H), 8.4 (s, 6H), 8.6 (s, 1H).

5.3.8: Synthesis of hexyl amide Pc 20

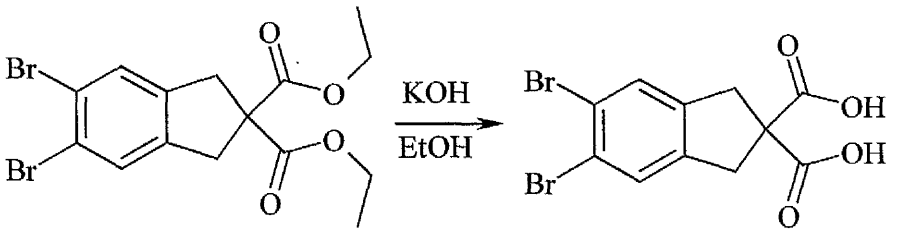


i) $ClCO_2Et$, NEt_3; ii) $H_2NC_6H_{13}$

The phthalocyanine (0.012 g, 0.009 mmol) was refluxed in a mixture of ethanol (10ml) and sodium hydroxide (20ml, 40 % w/w) for forty eight hours. The substrate was seen to dissolve in the solvent mixture over this period. The reaction mixture was allowed to cool to room temperature, and the ethanol removed under reduced pressure. The basic aqueous solution was treated with HCl (5M, 10 ml) and this caused the octa-acid to precipitate and be collected by filtration. The product was used directly in the next reaction: the solid was suspended in anhydrous acetone (10ml) at 0°C and triethylamine (0.009g, 0.09mmol) added, with stirring under nitrogen. After thirty minutes, ethyl chloroformate (0.009g, 0.09mmol) was added and the mixture stirred for a further thirty minutes. Hexylamine (0.009g, 0.09mmol) was transferred to the reaction vessel by syringe and the reaction heated to reflux for three hours.

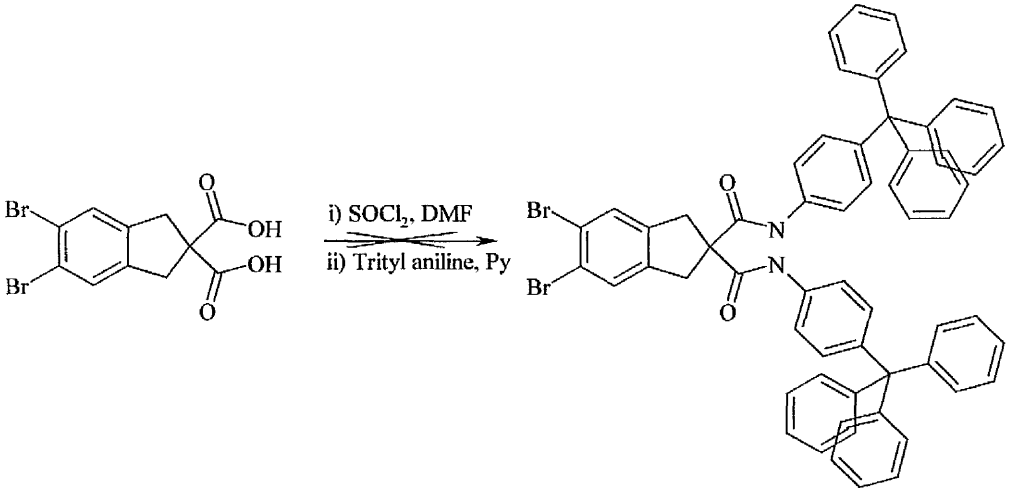
After cooling, the acetone was removed under reduced pressure. The residue was dissolved in ethyl acetate (20ml) and washed with hydrochloric acid (2M, aqueous, 3x20ml). The organic layer was collected, dried over magnesium sulfate, filtered and ethyl acetate removed under reduced pressure to give the product as a deep blue oil (0.006g, 40 %). *m/z* (MALDI) 1697 (M^+).

5.3.9: Synthesis of 5,6-dibromoindan-2,2-dicarboxylic acid 19



A suspension of the diester **14** (0.45g, 1.07mmol) was refluxed in a mixture of potassium hydroxide (10M aqueous, 10ml) and ethanol (5ml) for six hours. On completion of the reaction, the reaction mixture was allowed to cool and ethanol removed under reduced pressure. The aqueous was washed with DCM (2x50ml) and then acidified with HCl (11M, 20ml). The mixture was refrigerated overnight and the product **19** precipitated. This was collected by filtration as a white solid (0.11g, 28 %).

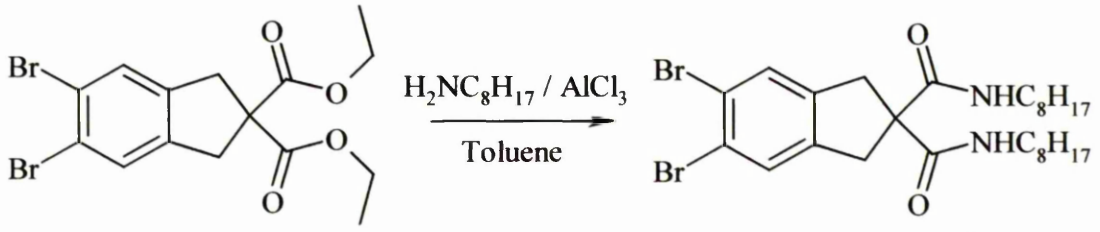
5.3.10: Attempted synthesis of 5,6-dibromoindan-2,2-dicarboxylic acid bis-[(4-trityl-phenyl)-amide]



The diacid **19** (0.11g, 0.3mmol) was dissolved in thionyl chloride (2ml) and dimethyl formamide (0.5ml), and the mixture heated to reflux for one hour under nitrogen. The excess thionyl chloride was removed via Dean-Stark apparatus to give a yellow solid.

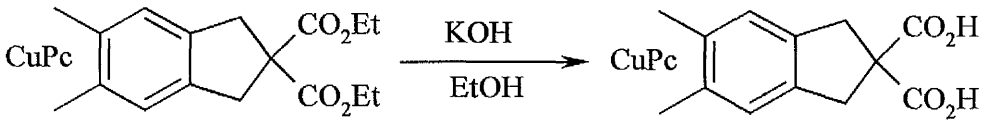
Trityl aniline (0.2g, 0.6mmol) in pyridine (1ml) and DMF (1ml) was added and the reaction mixture allowed to return to room temperature overnight. T.L.C (eluent: DCM) showed no sign of starting material, and the reaction was quenched with water 100ml) and the mixture filtered to give a red solid. No evidence of the desired amide could be found in either the solid or the filtrate, and thus the route was abandoned.

5.3.11: Attempted synthesis of 5,6-dibromoindan-2,2-dicarboxylic acid bis-octylamide



To a solution of 5,6-dibromoindan-2,2-dicarboxylic acid diethyl ester (0.67g, 1.6mmol) in toluene (50ml) was added octylamine (2.06g, 16mmol) and aluminium chloride (10mol.%, 0.021g). The reaction mixture was heated to reflux overnight. On cooling, analysis by T.L.C. (eluent: DCM) and mass spectrometry showed no evidence of product, and the method abandoned.

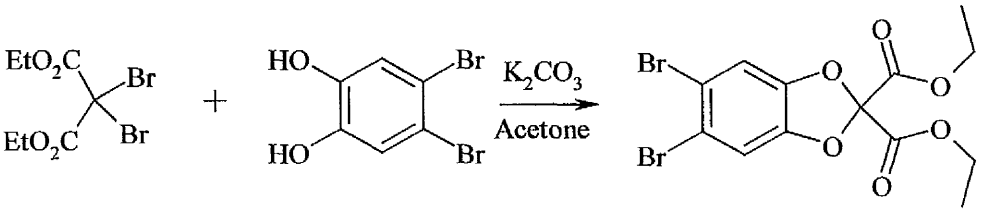
5.3.12: Synthesis of 'Octa acid' Pc 17



The octa ester, (0.1g, 0.08mmol) was suspended in potassium hydroxide solution (10M, 10ml) and ethanol (5ml), and the mixture refluxed for twenty four hours. After cooling to room temperature and removal of ethanol under reduced pressure, the aqueous solution was acidified with HCl (1M, 100ml) and the precipated octa acid collected by filtration (0.08g, 92 %), m/z (MALDI) 1088 ($M^+ + H$).

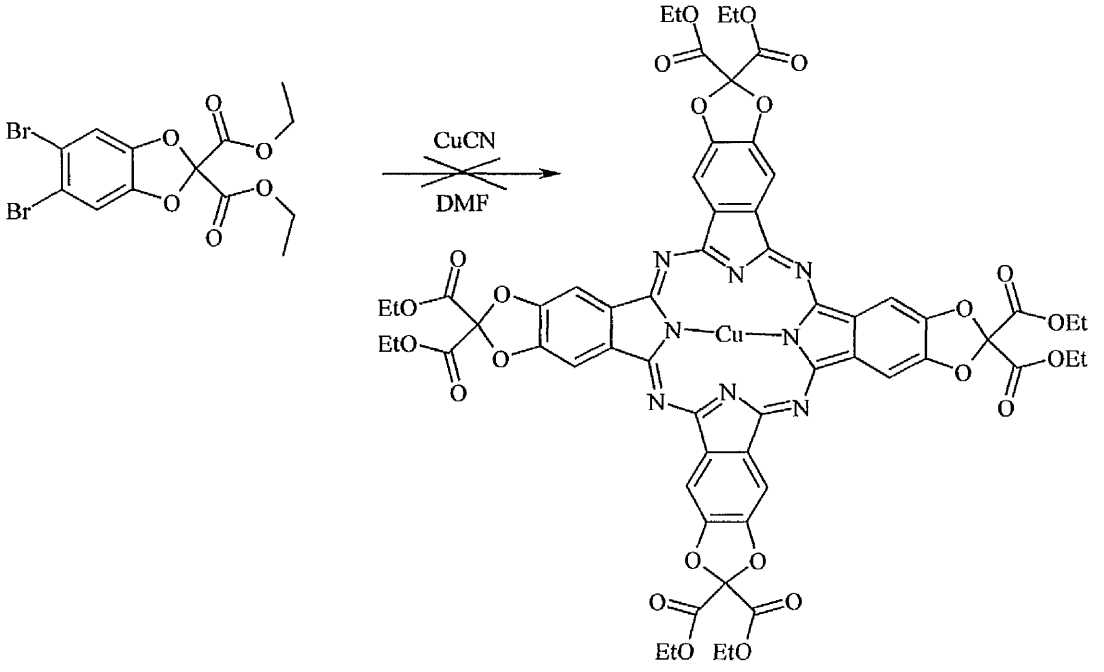
5.4: 'Ketal' Type Analogues of Indane Esters

5.4.1: Diethyl 5,6-dibromobenzo[1,3]dioxole-2,2-dicarboxylate 23



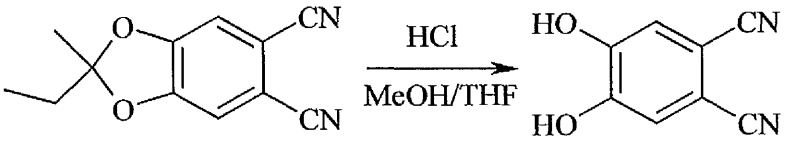
Potassium carbonate (2.06g, 14.9mmol) was suspended in anhydrous acetone (100ml). Dibromocatechol **22** (2g, 7.46mmol) and diethyl 2,2-dibromo malonate (4.74g, 14.9mmol) were added and the mixture stirred at room temperature for twenty four hours. Water (20ml) was added and the acetone removed under reduced pressure. The aqueous was extracted with diethyl ether (3x50ml). The ethereal extracts were washed with water, brine, dried over anhydrous magnesium sulfate and evaporated to give the crude material as an oil. Purification was achieved by bulb-to-bulb distillation, giving the product as a colourless oil (1.07g, 34 %), *m/z* (EI) 424 (M^+); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.36 (t, 6H), 4.40 (q, 4H), 7.24 (s, 2H).

5.4.2: Attempted synthesis of Pc derivative of diethyl 5,6-dibromobenzo[1,3]dioxole-2,2-dicarboxylate



Diethyl 5,6-dibromobenzo[1,3]dioxole-2,2-dicarboxylate (1g, 2.3mmol) was dissolved in anhydrous DMF (2ml) with stirring under nitrogen. Copper cyanide (4.22g, 47mmol) was added and the reaction vessel heated to 160°C for forty eight hours. No evidence of phthalocyanine formation was observed and the reaction was abandoned.

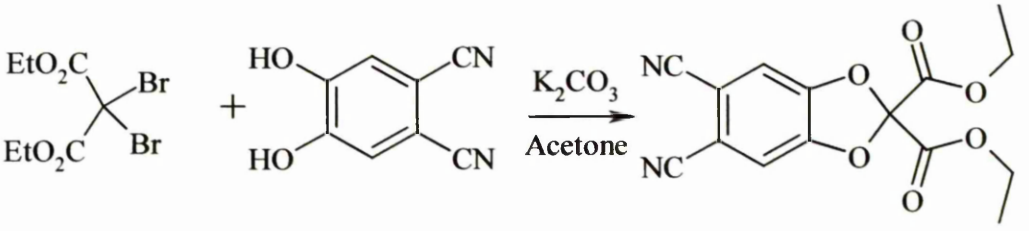
5.4.3: 4,5-dihydroxyphthalonitrile 24



A solution of the ketal 2-ethyl-2-methyl-benzo[1,3]dioxole-5,6-dicarbonitrile (1g, mmol) in 10%HCl/THF/MeOH (15ml:15ml:15ml) was refluxed under nitrogen for twenty four

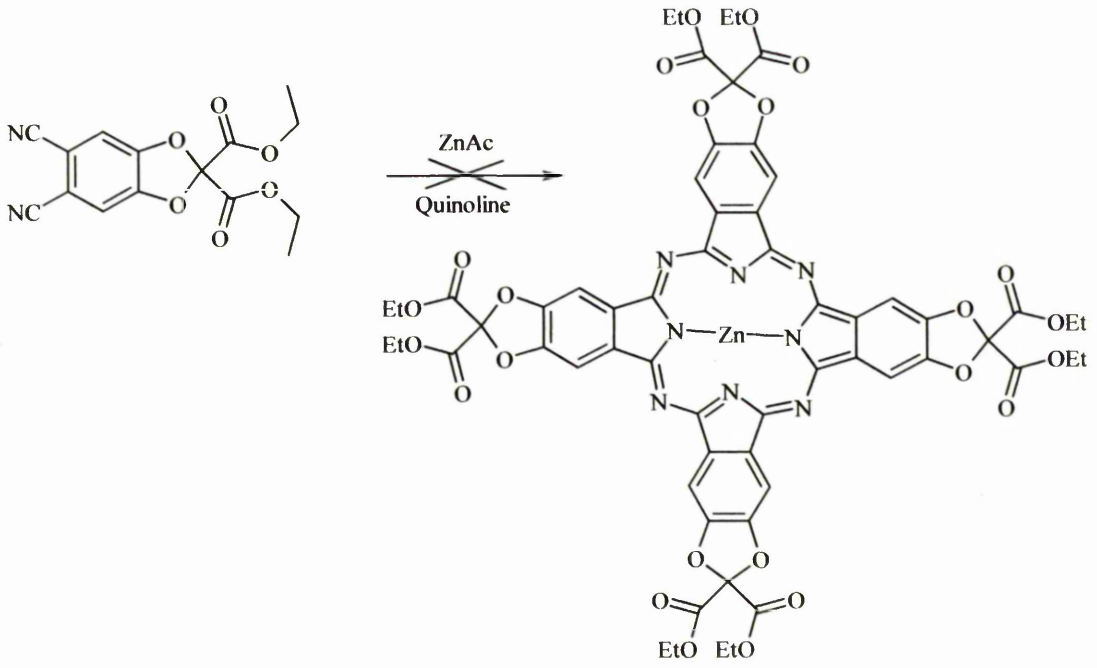
hours. It was then quenched into sodium carbonate (saturated solution, 100ml). The product precipitated and was collected by filtration and washed with water to remove inorganics, giving a white solid **24** (0.48g, 64 %), m/z (CI) 178 ($M^+ + NH_4^+$), 160 (M^+).

5.4.4: Diethyl 5,6-dicyanobenzo[1,3]dioxole-2,2-dicarboxylate 25



Potassium carbonate (0.83g, 6mmol) was suspended in anhydrous acetone (50ml). 4,5-Dihydroxy-phthalonitrile **24** (0.48g, 3mmol) and 2,2-dibromo diethyl malonate (1.8g, 5.7mmol) were added and the mixture stirred at room temperature for twenty four hours. Water (10ml) was added and the acetone removed under reduced pressure. The aqueous was extracted with diethyl ether (3x25ml). The ethereal extracts were washed with water, brine, dried over anhydrous magnesium sulfate and evaporated to give the crude material as an oil. Purification was achieved by column chromatography (eluent: DCM), giving the product **25** as a waxy solid (0.18g, 19 %), *m/z* (CI) 334 ($M^+ + NH4^+$), 316 (M^+); ^1H (300MHz, CDl_3): δ = 1.40 (t, 6H), 4.45 (q, 4H), 7.31 (s, 2H).

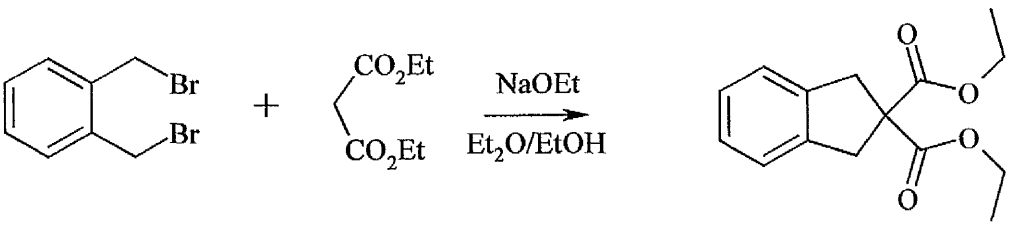
5.4.5: Attempted synthesis of phthalocyanine derivative of diethyl 5,6-dicyanobenzo[1,3]dioxole-2,2-dicarboxylate



A solution of the phthalonitrile (0.1g, 0.3mmol) in distilled quinoline (1ml) was stirred under nitrogen. To this was added zinc acetate (0.3g, 1.6mmol) and the reagents heated to 180°C for twenty four hours. No sign of formation of phthalocyanine was observed, thus the substrate was deemed not to cyclise under the reaction conditions and the reaction abandoned.

5.5: Hydrogen Bonded Supramolecular Chemistry

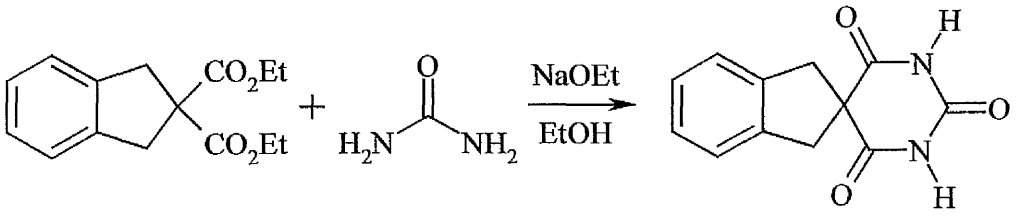
5.5.1: Diethyl indan-2,2-dicarboxylate 26



Sodium (1.3g, 56mmol), was dissolved in ethanol (10ml) and anhydrous diethyl ether (100ml) added under nitrogen. Diethyl malonate (2.8g, 17mmol) was then added by syringe and the mixture stirred for thirty minutes. 1,2-bis(bromomethyl) benzene (5g, 19mmol) in anhydrous diethyl ether (50ml) was transferred to the reaction vessel via syringe. The reagents were then heated to reflux for five hours. The reaction was followed by T.L.C. (eluent: 5:1 40/60 petrol:EtOAc)

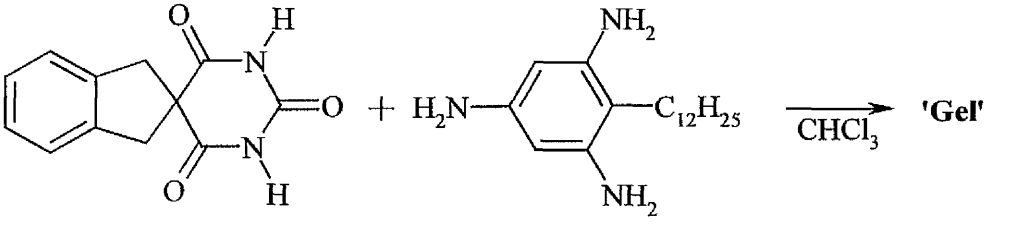
When the reaction was shown to be complete, the vessel was allowed to cool to room temperature, and $HCl_{(aq)}$ (1M, 100ml) was added. The organic phase was separated and the aqueous phase washed with diethyl ether (3x50ml). The combined organics were dried over magnesium sulfate, filtered and solvent removed under reduced pressure to give the crude product as a yellow oil. The crude material was purified by column chromatography (eluent as T.L.C) to give the diester **26** as a white solid (2g, 40 %), *m/z* (EI) 262 (M^+); ^1H NMR (300 MHz, $CDCl_3$): δ = 1.24 (t, 6H), 3.61 (s, 4H), 4.21 (q, 4H), 7.20 (m, 4H).

5.5.2: Synthesis of barbiturate derivative (5-indan) barbituric acid 27



The diester **26** (1g, 3.8mmol) and urea (0.27g, 4.6mmol) were added to an ethanolic sodium ethoxide solution (0.19g Na in 10ml EtOH) and the resultant solution heated under reflux for forty eight hours. The reaction vessel was then allowed to cool to room temperature, and solvent removed under reduced pressure. The residues were taken up in water (50ml) and HCl (1M, 100ml) added. The aqueous was then extracted with ethyl acetate (5x25ml) and the organics dried over magnesium sulfate, filtered and solvent removed under reduced pressure to give the crude product as a white solid. This was purified by recrystallisation (EtOH) to give the product **27** (0.82g, 93 %). Mp. 289 ° C (decomposed), *m/z* (CI) 248 ($M^+ + NH_4^+$), 230 (M^+); 1H NMR (300 MHz, d_5-pyridine): δ = 3.82 (s, 4H), 7.20 (s, 4H), 13.42 (s, broad, 2 NH); (Calc. for $C_{12}H_{10}N_2O_3$: C, 62.61; H, 4.38; N, 12.17. Found: C, 62.58; H, 4.29; N, 12.06 %).

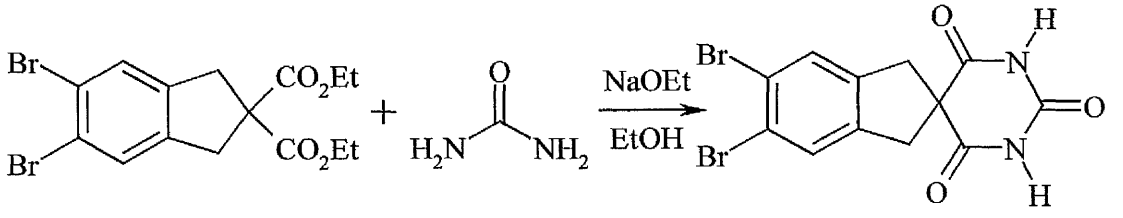
5.5.3: 'Gelling' of Barbiturate and 5-dodecyl-2,4,6-triaminopyrimidine



The two reagents (0.023g of each, approx 0.1mmol) were heated in chloroform (1ml) until they dissolved. They were then allowed to cool to room temperature, and a gel was seen to

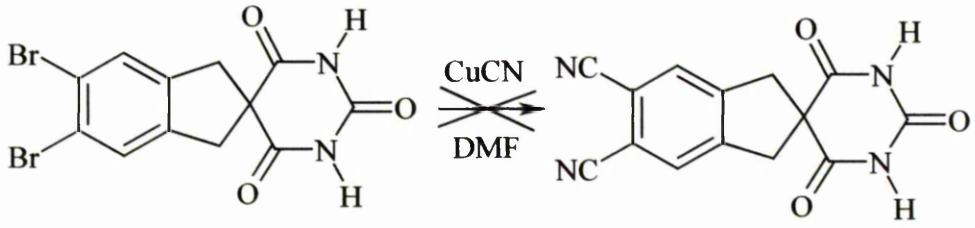
form. On removal of solvent under reduced pressure and dissolution in deuterated pyridine, the NMR behaviour of the mixed materials was studied. 5-dodecyl-2,4,6-triaminopyrimidine ^{1}H NMR (300 MHz, d_5-pyridine): δ = 0.82, (t, 3H), 1.14 (m, 16H), 1.25 (m. 2H), 1.65 (dt, 2H), 2.62 (t, 2H), 6.08 (s, 2H), 6.26 (s, 4H). Mixed 'gel' ^{1}H NMR (300 MHz, d_5-pyridine): δ = 0.82, (t, 3H), 1.20 (m, 16H), 1.33 (m, 2H), 1.67 (dt, 2H), 2.66 (t, 2H), 3.82, (s, 4H), 5.22 (s, 2H), 6.46 (s, 2H), 6.49 (s, 4H), 7.20 (s, 4H).

5.5.4: Synthesis of barbiturate derivative (5-indan) barbituric acid



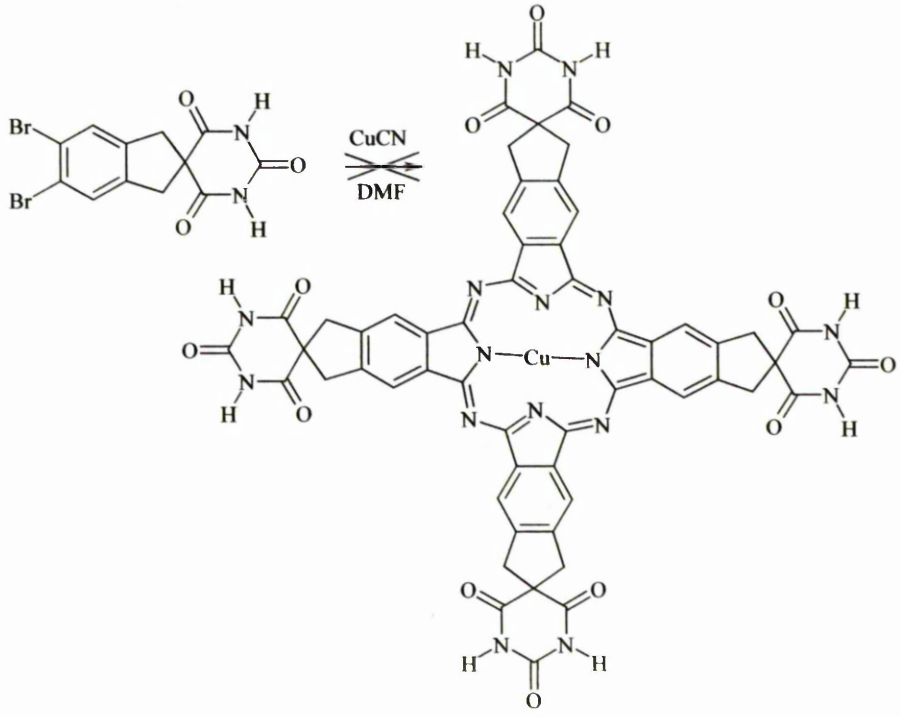
The diester (0.25g, 0.6mmol) and urea (0.044g, 0.72mmol) were added to an ethanolic sodium ethoxide solution (0.1g, 1.32mmol NaOEt in 10ml EtOH) and the resultant solution heated under reflux for forty eight hours. The reaction vessel was then allowed to cool to room temperature, and solvent removed under reduced pressure. The residues were taken up in water (50ml) and HCl (1M, 100ml) added. The aqueous was then extracted with ethyl acetate (5x25ml) and the organics dried over magnesium sulfate, filtered and solvent removed under reduced pressure to give the crude product as a white solid. This was purified by recrystallisation (EtOH) to give the product (0.212g, 92 %), *m/z* (CI) 386 (M^+); ^{1}H NMR (300 MHz, d_6-DMSO): δ = 3.40 (s, 4H), 7.68 (s, 2H).

5.5.5: Attempted cyanation of the dibromo barbituric acid



Copper cyanide (0.59g, 6.6mmol) was added to a stirred solution of the dibromide (0.85g, 2.2mmol) in anhydrous DMF (10ml). The reaction mixture was heated to 160°C for twenty four hours. Mass spectrometry of a sample of the reaction mixture showed no evidence of starting material or product, and the reaction was abandoned.

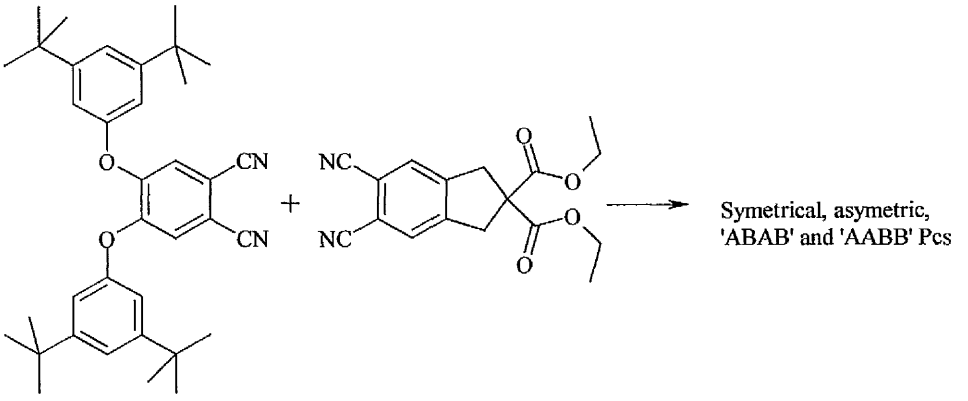
5.5.6: Attempted cyclisation of the dibromo barbituric acid



Copper cyanide (0.93g, 10.4mmol) was added to a stirred solution of the dibromide (0.0.2g, 0.52mmol) in anhydrous DMF (1.4ml). The reaction mixture was heated to 180°C

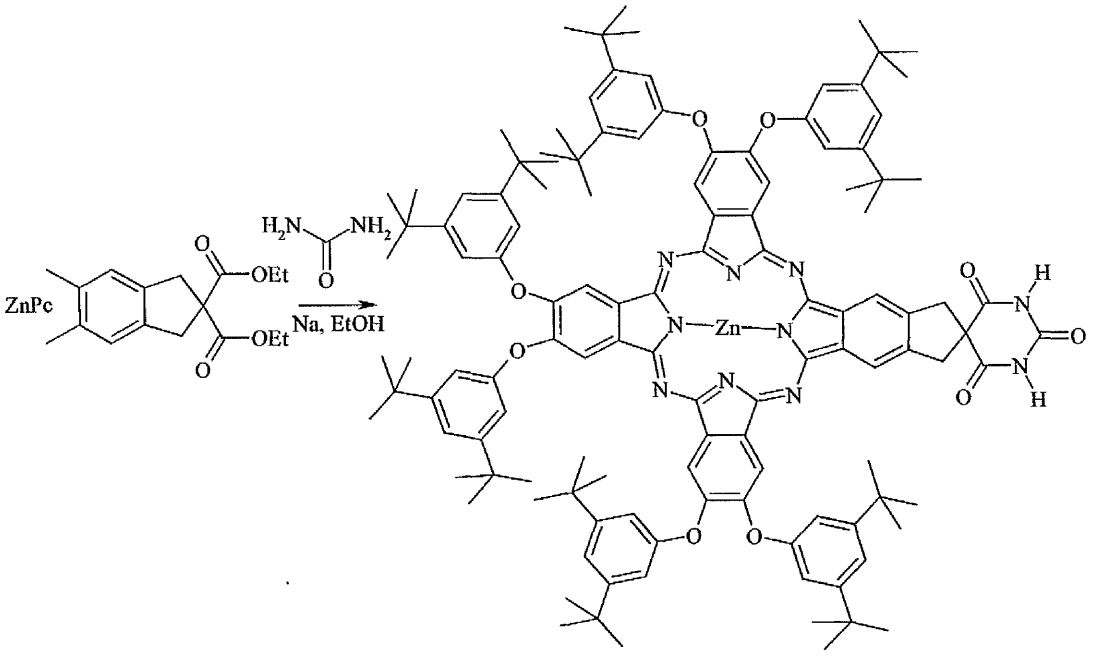
for 36 hours. Mass spectrometry of a sample of the reaction mixture showed no evidence of starting material or cyclised product, and the reaction was abandoned.

5.5.7: Synthesis of asymmetric pc 28



A solution of the two phthalonitriles (4,5-bis-(3,5-di-tert-butyl-phenoxy)-phthalonitrile: 0.5 g, 0.93mmol, diethyl 5,6-dicyanoindan-2,2-dicarboxylate (**15**): 0.13g, 0.31mmol) in distilled quinoline (2ml) was stirred under nitrogen. To this was added anhydrous zinc acetate (0.23g, 1.2mmol) and the reagents heated to 180°C for twenty four hours. Formation of the characteristic deep green zinc phthalocyanine was observed. The mixture was poured into methanol (20ml) and the products precipitated. The mixture was isolated by filtration, and separation achieved by flash column chromatography (eluent: 10:1 40/60 petrol:EtOAc) giving the symmetrical alkoxy Pc (0.3g), *m/z* (MALDI) 2226 (M^+), the asymmetrical 'mixed' Pc (0.14g), *m/z* (MALDI) 1985 (M^+),^{1}H NMR (300 MHz, d_5-pyridine): δ = 1.2 (m, 114H), 3.8 (s,4H), 4.4 (q, 4H), 8.2 (s, 12H), 8.25 (s, 6H), 8.4 (s, 6H), 8.6 (s, 1H), and the two 'AABB and ABAB' isomers (0.01g), *m/z* (MALDI) 1760 (M^+).

5.5.8: Synthesis of Pc Barbiturate 29



The diester Pc **28** (0.14g, 0.07mmol) and urea (0.005g, 0.085mmol) were added to an ethanolic sodium ethoxide solution (0.004g Na in 5ml EtOH) and the resultant solution heated under reflux for forty eight hours. The reaction vessel was then allowed to cool to room temperature, and solvent removed under reduced pressure. The residues were taken up in water (20ml) and HCl (1M, 10ml) added. The aqueous was then extracted with ethyl acetate (5x10ml) and the organics dried over magnesium sulfate, filtered and solvent removed under reduced pressure to give the crude product as a deep green solid. This was purified by recrystallisation (EtOH) to give the product (0.12 g, 90 %). *m/z* (MALDI) 1953 (M^+). ^{1}H NMR (300 MHz, d_5-pyridine): δ = 1.2 (m, 108H), 3.8 (s, 4H), 8.2 (s, 12H), 8.25 (s, 6H), 8.4 (s, 6H), 8.6 (s, 1H).

6.0: Appendix – Crystallographic Data

27 Nov 2000

Acta Cryst. (1999). C55, 000–000

ENTER SECTION TITLE

FIRST AUTHORS NAME

FIRST AUTHORS ADDRESS. E-mail: enter email address

Abstract

ENTER ABSTRACT

Comment

ENTER TEXT

Experimental

ENTER EXPERIMENTAL SECTION

Crystal data

$C_{62}H_{128}N_8$
$M_r = 1346.02$
Triclinic
$P\overline{1}$
$a = 15.7306(16)$ Å
$b = 20.621(3)$ Å
$c = 21.527(4)$ Å
$\alpha = 62.462(10)°$
$\beta = 82.358(17)°$
$\gamma = 86.470(13)°$
$V = 6136.7(15)$ Å^3
$Z = 3$
$D_x = 1.093$ Mg m^{-3}
D_m not measured

synchrotron radiation
$\lambda = 0.68740$ Å
Cell parameters from 29566 reflections
$\theta = 3–25.64°$
$\mu = 0.063$ mm^{-1}
$T = 150(2)$ K
Plate
Green
0.42 × 0.12 × 0.01 mm

Data collection

Siemens SMART diffractometer	13971 reflections with
ω scans	>2sigma(I)
Absorption correction:	$R_{int} = 0.0875$
multiscan (SADABS; Blessing, 1995)	$\theta_{max} = 26.41°$
$T_{min} = 0.59$, $T_{max} = 1.00$	$h = -19 \rightarrow 19$
49123 measured reflections	$k = -24 \rightarrow 25$
24390 independent reflections	$l = -26 \rightarrow 26$

Refinement

Refinement on F^2	$w=1/[\sigma^2(F_o^2) + (0.1663P)^2 + 11.0470P]$
$R(F) = 0.1293$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.3610$	$(\Delta/\sigma)_{max} = 0.003$
$S = 1.037$	$\Delta\rho_{max} = 0.729$ e Å^{-3}
24390 reflections	$\Delta\rho_{min} = -0.447$ e Å^{-3}
1347 parameters	Extinction correction: none
H atoms treated by a mixture of independent and constrained refinement	Scattering factors from *International Tables for Crystallography* (Vol. C)

The data were collected at Station 9.8 at Daresbury. The asymmetric unit consists of one whole molecule, together with a half molecule where the complete molecule is generated by inversion. There is disorder in some of the C6 chains, such that some atoms or chains of atoms are disordered over two sites, A and B, with occupancies constrained to sum to one. These atoms were C49, C53 - c55 C66 - C68, C73, C118 - C120, and C136 - C138. The disordered atoms were refined isotropically. All other non H atoms were refined anisotropically, and H atoms were included in calculated positions.

Data collection: Siemens XSCANS. Cell refinement: Siemens XSCANS. Data reduction: Siemens *SHELXTL*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Software used to prepare material for publication teXsan (MSC, 1995).

ENTER ACKNOWLEDGEMENTS

Supplementary data for this paper are available from the IUCr electronic archives (Reference: PRINTCIF). Services for accessing these data are described at the back of the journal.

References

ENTER OTHER REFERENCES

Molecular Structure Corporation. (1995). teXsan. Single Crystal Structure Analysis Software. Version 1.7. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

ENTER FIGURE CAPTIONS

ENTER TABLE LEGENDS

Supplementary data

The tables of data shown below are not normally printed in *Acta Cryst. Section C* but the data will be available electronically *via* the online contents pages at

http://journals.iucr.org/c/journalhomepage.html

Specific tables may be included in the printed manuscript at the discretion of the Co-editor. If you wish to include any of the following tables in your paper, please state which tables are required in the _publ_contact_letter field of the CIF. In the case of tables of atomic coordinates, please state whether you wish the coordinates of any H atoms to be included.

Table 51. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a^i a^j \mathbf{a}_i.\mathbf{a}_j .$$

	Occupancy	x	y	z	U_{eq}
N1	1	0.6925 (2)	0.56044 (17)	0.49755 (16)	0.0237 (7)
N2	1	0.5805 (2)	0.58991 (17)	0.42030 (17)	0.0256 (7)
N3	1	0.6056 (2)	0.45926 (17)	0.47639 (17)	0.0258 (7)
N4	1	0.5875 (2)	0.33053 (18)	0.51352 (18)	0.0297 (8)
N5	1	0.6917 (2)	0.34798 (17)	0.57763 (18)	0.0288 (8)
N6	1	0.7947 (2)	0.3179 (2)	0.6614 (2)	0.0362 (9)
N7	1	0.7839 (2)	0.45065 (18)	0.59450 (17)	0.0271 (7)
N8	1	0.8034 (2)	0.57944 (18)	0.55633 (17)	0.0271 (7)
C1	1	0.7433 (2)	0.6018 (2)	0.5123 (2)	0.0246 (8)
C2	1	0.7222 (3)	0.6797 (2)	0.4724 (2)	0.0283 (9)
C3	1	0.7585 (3)	0.7427 (2)	0.4643 (2)	0.0342 (10)
H3	1	0.8050	0.7412	0.4875	0.041
C4	1	0.7227 (3)	0.8086 (2)	0.4197 (3)	0.0406 (11)
C5	1	0.7479 (4)	0.8858 (3)	0.4004 (3)	0.0537 (14)
H5A	1	0.8097	0.8916	0.3910	0.064
H5B	1	0.7271	0.8981	0.4381	0.064
C6	1	0.7039 (4)	0.9354 (3)	0.3519 (3)	0.0567 (15)
C7	1	0.6241 (3)	0.8888 (2)	0.3422 (3)	0.0491 (13)
H7A	1	0.5753	0.9014	0.3672	0.059
H7B	1	0.6089	0.8966	0.2970	0.059
C8	1	0.6514 (3)	0.8104 (2)	0.3852 (3)	0.0381 (11)
C9	1	0.6161 (3)	0.7475 (2)	0.3918 (2)	0.0293 (9)
H9	1	0.5699	0.7489	0.3684	0.035
C10	1	0.6539 (3)	0.6813 (2)	0.4359 (2)	0.0284 (9)
C11	1	0.6389 (2)	0.6066 (2)	0.45106 (19)	0.0222 (8)
C12	1	0.5670 (3)	0.5230 (2)	0.4315 (2)	0.0265 (9)
C13	1	0.5070 (3)	0.5033 (2)	0.3965 (2)	0.0263 (9)
C14	1	0.4536 (3)	0.5460 (2)	0.3462 (2)	0.0259 (9)
H14	1	0.4489	0.5964	0.3286	0.031
C15	1	0.4082 (3)	0.5087 (2)	0.3206 (2)	0.0290 (9)
C16	1	0.3538 (3)	0.5399 (2)	0.2602 (2)	0.0334 (10)
H16A	1	0.3792	0.5842	0.2215	0.040
H16B	1	0.2963	0.5508	0.2754	0.040
C17	1	0.3524 (3)	0.4779 (3)	0.2381 (2)	0.0353 (10)
C18	1	0.3592 (3)	0.4081 (2)	0.3083 (2)	0.0308 (9)
H18A	1	0.3029	0.3914	0.3341	0.037
H18B	1	0.3876	0.3691	0.3002	0.037
C19	1	0.4121 (3)	0.4323 (2)	0.3476 (2)	0.0287 (9)
C20	1	0.4629 (3)	0.3899 (2)	0.4000 (2)	0.0262 (9)
H20	1	0.4646	0.3393	0.4186	0.031
C21	1	0.5117 (3)	0.4269 (2)	0.4236 (2)	0.0248 (8)
C22	1	0.5722 (2)	0.4010 (2)	0.4744 (2)	0.0262 (9)
C23	1	0.6406 (3)	0.3069 (2)	0.5632 (2)	0.0314 (9)
C24	1	0.6516 (3)	0.2293 (2)	0.6108 (3)	0.0397 (11)
C25	1	0.6110 (3)	0.1667 (2)	0.6190 (3)	0.0474 (13)

H25	1	0.5706	0.1692	0.5901	0.057
C26	1	0.6351 (4)	0.1009 (3)	0.6728 (3)	0.0555 (15)
C27	1	0.6025 (4)	0.0243 (3)	0.6954 (4)	0.0714 (19)
H27A	1	0.6303	0.0047	0.6647	0.086
H27B	1	0.5409	0.0244	0.6947	0.086
C28	1	0.6261 (5)	−0.0202 (3)	0.7706 (4)	0.078 (2)
C29	1	0.7069 (5)	0.0185 (3)	0.7702 (4)	0.080 (2)
H29A	1	0.7105	0.0146	0.8164	0.097
H29B	1	0.7583	−0.0024	0.7563	0.097
C30	1	0.6957 (4)	0.0976 (3)	0.7164 (3)	0.0619 (17)
C31	1	0.7355 (3)	0.1586 (3)	0.7080 (3)	0.0567 (16)
H31	1	0.7767	0.1558	0.7364	0.068
C32	1	0.7114 (3)	0.2258 (3)	0.6543 (3)	0.0429 (12)
C33	1	0.7368 (3)	0.3009 (2)	0.6323 (2)	0.0351 (10)
C34	1	0.8165 (3)	0.3863 (2)	0.6429 (2)	0.0295 (9)
C35	1	0.8797 (3)	0.4044 (2)	0.6751 (2)	0.0326 (10)
C36	1	0.9288 (3)	0.3581 (3)	0.7285 (2)	0.0335 (10)
H36	1	0.9262	0.3074	0.7474	0.040
C37	1	0.9814 (3)	0.3916 (3)	0.7517 (2)	0.0355 (10)
C38	1	1.0384 (3)	0.3564 (3)	0.8093 (2)	0.0404 (11)
H38A	1	1.0937	0.3440	0.7917	0.049
H38B	1	1.0123	0.3126	0.8480	0.049
C39	1	1.0476 (3)	0.4155 (3)	0.8325 (3)	0.0419 (11)
C40	1	1.0450 (3)	0.4870 (3)	0.7613 (3)	0.0404 (11)
H40A	1	1.0228	0.5277	0.7695	0.048
H40B	1	1.1017	0.4995	0.7351	0.048
C41	1	0.9856 (3)	0.4683 (3)	0.7224 (2)	0.0367 (11)
C42	1	0.9373 (3)	0.5144 (2)	0.6685 (2)	0.0314 (9)
H42	1	0.9406	0.5651	0.6489	0.038
C43	1	0.8839 (3)	0.4804 (2)	0.6455 (2)	0.0324 (10)
C44	1	0.8211 (3)	0.5089 (2)	0.5943 (2)	0.0300 (9)
C45	1	0.6809 (4)	1.0127 (3)	0.3228 (4)	0.0721 (19)
H45A	1	0.7338	1.0376	0.3174	0.087
H45B	1	0.6554	1.0392	0.2792	0.087
C46	1	0.6232 (5)	1.0178 (4)	0.3789 (4)	0.081 (2)
H46A	1	0.6504	0.9956	0.4220	0.097
H46B	1	0.5715	0.9902	0.3872	0.097
C47	1	0.5977 (5)	1.0989 (4)	0.3620 (5)	0.092 (2)
H47A	1	0.6495	1.1264	0.3537	0.111
H47B	1	0.5707	1.1211	0.3188	0.111
C48	1	0.5404 (6)	1.1049 (4)	0.4170 (6)	0.105 (3)
H48A	1	0.5566	1.0669	0.4614	0.126
H48B	1	0.4836	1.0925	0.4130	0.126
C49A	0.45 (3)	0.5318 (13)	1.1740 (9)	0.4236 (13)	0.090 (8)
H49A	0.45 (3)	0.5757	1.1752	0.4508	0.108
H49B	0.45 (3)	0.5412	1.2153	0.3770	0.108
C49B	0.55 (3)	0.4944 (11)	1.1808 (7)	0.3932 (8)	0.081 (6)
H49C	0.55 (3)	0.5361	1.2202	0.3706	0.097
H49D	0.55 (3)	0.4545	1.1874	0.3601	0.097
C50	1	0.4480 (8)	1.1811 (5)	0.4576 (6)	0.157 (5)
H50A	1	0.4448	1.2270	0.4592	0.235
H50B	1	0.4397	1.1418	0.5048	0.235
H50C	1	0.4043	1.1793	0.4314	0.235
C51	1	0.7641 (4)	0.9393 (4)	0.2667 (4)	0.0705 (18)
H51A	1	0.7800	0.8897	0.2763	0.085
H51B	1	0.7308	0.9587	0.2270	0.085
C52	1	0.8450 (5)	0.9835 (5)	0.2439 (5)	0.105 (3)
H52A	1	0.8688	0.9786	0.2851	0.125
H52B	1	0.8320	1.0347	0.2155	0.125
C53A	0.661 (12)	0.9120 (8)	0.9571 (7)	0.2003 (7)	0.096 (3)
H53A	0.661 (12)	0.8826	0.9381	0.1752	0.115
H53B	0.661 (12)	0.9473	0.9980	0.1658	0.115
C54A	0.661 (12)	0.9688 (7)	0.8971 (6)	0.2494 (6)	0.083 (4)
H54A	0.661 (12)	0.9310	0.8625	0.2888	0.100
H54B	0.661 (12)	1.0030	0.9199	0.2683	0.100

C55A	0.661 (12)	1.0305 (9)	0.8526 (7)	0.2224 (8)	0.105 (5)
H55A	0.661 (12)	1.0651	0.8198	0.2587	0.126
H55B	0.661 (12)	0.9993	0.8241	0.2075	0.126
C53B	0.339 (12)	0.8925 (15)	1.0006 (11)	0.1740 (11)	0.096 (3)
H53C	0.339 (12)	0.9403	1.0325	0.1650	0.115
H53D	0.339 (12)	0.8549	1.0265	0.1378	0.115
C54B	0.339 (12)	0.9256 (12)	0.9320 (11)	0.1701 (11)	0.077 (7)
H54C	0.339 (12)	0.9426	0.9440	0.1210	0.093
H54D	0.339 (12)	0.8792	0.8968	0.1877	0.093
C55B	0.339 (12)	1.0021 (15)	0.896 (2)	0.2118 (15)	0.169 (16)
H55C	0.339 (12)	1.0081	0.9163	0.2434	0.203
H55D	0.339 (12)	0.9914	0.8438	0.2401	0.203
C56	1	1.0837 (12)	0.9075 (14)	0.1630 (11)	0.46 (3)
H56A	1	1.1255	0.8838	0.1436	0.691
H56B	1	1.1123	0.9361	0.1787	0.691
H56C	1	1.0483	0.9387	0.1276	0.691
C57	1	0.2678 (3)	0.4789 (3)	0.2081 (3)	0.0411 (11)
H57A	1	0.2202	0.4792	0.2415	0.049
H57B	1	0.2654	0.5242	0.1648	0.049
C58	1	0.2556 (3)	0.4157 (3)	0.1927 (3)	0.0452 (12)
H58A	1	0.2575	0.3703	0.2358	0.054
H58B	1	0.3028	0.4153	0.1589	0.054
C59	1	0.1715 (3)	0.4192 (3)	0.1634 (3)	0.0498 (13)
H59A	1	0.1700	0.4646	0.1201	0.060
H59B	1	0.1245	0.4205	0.1969	0.060
C60	1	0.1569 (4)	0.3558 (4)	0.1482 (4)	0.0633 (16)
H60A	1	0.1525	0.3109	0.1923	0.076
H60B	1	0.2066	0.3514	0.1184	0.076
C61	1	0.0770 (5)	0.3634 (5)	0.1121 (4)	0.083 (2)
H61A	1	0.0796	0.4099	0.0697	0.099
H61B	1	0.0776	0.3250	0.0980	0.099
C62	1	−0.0048 (5)	0.3595 (5)	0.1561 (5)	0.103 (3)
H62A	1	−0.0056	0.3162	0.2006	0.155
H62B	1	−0.0516	0.3580	0.1324	0.155
H62C	1	−0.0105	0.4018	0.1640	0.155
C63	1	0.4294 (3)	0.4870 (3)	0.1819 (3)	0.0476 (12)
H63A	1	0.4288	0.4455	0.1722	0.057
H63B	1	0.4187	0.5302	0.1389	0.057
C64	1	0.5206 (4)	0.4935 (4)	0.1962 (3)	0.0722 (19)
H64A	1	0.5541	0.5232	0.1513	0.087
H64B	1	0.5177	0.5196	0.2241	0.087
C65	1	0.5684 (4)	0.4222 (5)	0.2339 (4)	0.090 (2)
H65A	1	0.5876	0.4012	0.2022	0.108
H65B	1	0.5323	0.3869	0.2742	0.108
C66A	0.609 (12)	0.6485 (7)	0.4452 (7)	0.2583 (6)	0.070 (3)
H66A	0.609 (12)	0.6870	0.4762	0.2173	0.085
H66B	0.609 (12)	0.6285	0.4725	0.2840	0.085
C67A	0.609 (12)	0.6953 (9)	0.3774 (8)	0.3049 (7)	0.101 (5)
H67A	0.609 (12)	0.6579	0.3491	0.3479	0.121
H67B	0.609 (12)	0.7451	0.3917	0.3178	0.121
C68A	0.609 (12)	0.7241 (13)	0.3296 (9)	0.2696 (10)	0.123 (7)
H68A	0.609 (12)	0.7533	0.2873	0.3013	0.185
H68B	0.609 (12)	0.7624	0.3568	0.2276	0.185
H68C	0.609 (12)	0.6750	0.3144	0.2574	0.185
C66B	0.391 (12)	0.6567 (9)	0.4100 (10)	0.2513 (10)	0.070 (3)
H66C	0.391 (12)	0.6638	0.4396	0.2746	0.085
H66D	0.391 (12)	0.6930	0.4319	0.2066	0.085
C67B	0.391 (12)	0.6960 (13)	0.3379 (12)	0.2940 (15)	0.101 (8)
H67C	0.391 (12)	0.6805	0.3028	0.2793	0.121
H67D	0.391 (12)	0.6742	0.3203	0.3434	0.121
C68B	0.391 (12)	0.7926 (13)	0.3447 (14)	0.2848 (13)	0.114 (9)
H68D	0.391 (12)	0.8171	0.2979	0.3128	0.170
H68E	0.391 (12)	0.8079	0.3793	0.2998	0.170
H68F	0.391 (12)	0.8141	0.3613	0.2361	0.170
C69	1	0.6447 (6)	−0.1017 (3)	0.7881 (5)	0.099 (3)

H69A	1	0.6953	−0.1031	0.7575	0.118
H69B	1	0.6586	−0.1276	0.8362	0.118
C70	1	0.5750 (7)	−0.1421 (4)	0.7807 (7)	0.144 (4)
H70A	1	0.5629	−0.1176	0.7321	0.172
H70B	1	0.5237	−0.1391	0.8097	0.172
C71	1	0.5934 (9)	−0.2251 (5)	0.8016 (7)	0.153 (5)
H71A	1	0.5488	−0.2447	0.7880	0.184
H71B	1	0.6479	−0.2300	0.7771	0.184
C72	1	0.5959 (10)	−0.2671 (5)	0.8809 (7)	0.202 (8)
H72A	1	0.6540	−0.2860	0.8816	0.243
H72B	1	0.5604	−0.3086	0.8914	0.243
C73A	0.227 (14)	0.581 (2)	−0.268 (3)	0.964 (3)	0.136 (5)
H73A	0.227 (14)	0.6299	−0.2891	0.9902	0.163
H73B	0.227 (14)	0.5705	−0.2192	0.9599	0.163
C73B	0.773 (14)	0.4984 (10)	−0.2723 (9)	0.9206 (8)	0.136 (5)
H73C	0.773 (14)	0.4759	−0.2237	0.9091	0.163
H73D	0.773 (14)	0.4609	−0.2966	0.9056	0.163
C74	1	0.5031 (12)	−0.3155 (8)	0.9992 (8)	0.219 (8)
H74A	1	0.4576	−0.2880	1.0105	0.329
H74B	1	0.5166	−0.3571	1.0417	0.329
H74C	1	0.4852	−0.3317	0.9678	0.329
C75	1	0.5521 (6)	−0.0115 (4)	0.8204 (4)	0.094 (3)
H75A	1	0.5492	0.0395	0.8103	0.113
H75B	1	0.4990	−0.0230	0.8094	0.113
C76	1	0.5564 (8)	−0.0556 (6)	0.8957 (6)	0.133 (4)
H76A	1	0.6119	−0.0488	0.9068	0.160
H76B	1	0.5510	−0.1069	0.9079	0.160
C77	1	0.4870 (9)	−0.0359 (6)	0.9394 (7)	0.143 (4)
H77A	1	0.4933	−0.0667	0.9888	0.171
H77B	1	0.4959	0.0143	0.9295	0.171
C78	1	0.3977 (8)	−0.0429 (7)	0.9282 (7)	0.146 (4)
H78A	1	0.3911	−0.0901	0.9297	0.175
H78B	1	0.3874	−0.0054	0.8815	0.175
C79	1	0.3309 (9)	−0.0358 (7)	0.9823 (8)	0.214 (8)
H79A	1	0.3408	−0.0737	1.0289	0.257
H79B	1	0.3382	0.0111	0.9813	0.257
C80	1	0.2417 (8)	−0.0415 (8)	0.9712 (8)	0.192 (7)
H80A	1	0.2030	−0.0372	1.0076	0.289
H80B	1	0.2335	−0.0880	0.9727	0.289
H80C	1	0.2305	−0.0030	0.9260	0.289
C81	1	0.9689 (3)	0.4135 (3)	0.8847 (3)	0.0474 (12)
H81A	1	0.9720	0.4556	0.8931	0.057
H81B	1	0.9177	0.4191	0.8619	0.057
C82	1	0.9577 (4)	0.3453 (3)	0.9563 (3)	0.0593 (15)
H82A	1	0.9589	0.3022	0.9489	0.071
H82B	1	1.0053	0.3418	0.9820	0.071
C83	1	0.8741 (5)	0.3464 (4)	1.0001 (3)	0.078 (2)
H83A	1	0.8277	0.3577	0.9712	0.094
H83B	1	0.8769	0.3854	1.0130	0.094
C84	1	0.8530 (5)	0.2745 (4)	1.0676 (4)	0.089 (2)
H84A	1	0.8550	0.2349	1.0550	0.107
H84B	1	0.8973	0.2653	1.0981	0.107
C85	1	0.7672 (8)	0.2728 (7)	1.1088 (5)	0.157 (5)
H85A	1	0.7684	0.3081	1.1266	0.189
H85B	1	0.7241	0.2890	1.0764	0.189
C86	1	0.7404 (9)	0.2043 (7)	1.1665 (7)	0.216 (8)
H86A	1	0.7473	0.1669	1.1516	0.324
H86B	1	0.6811	0.2073	1.1829	0.324
H86C	1	0.7746	0.1926	1.2041	0.324
C87	1	1.1323 (3)	0.4052 (3)	0.8654 (3)	0.0480 (13)
H87A	1	1.1322	0.3566	0.9049	0.058
H87B	1	1.1796	0.4074	0.8306	0.058
C88	1	1.1495 (3)	0.4595 (3)	0.8909 (3)	0.0527 (14)
H88A	1	1.1008	0.4607	0.9231	0.063
H88B	1	1.1561	0.5079	0.8510	0.063

C89	1	1.2308 (4)	0.4398 (4)	0.9286 (3)	0.0642 (16)
H89A	1	1.2214	0.3939	0.9714	0.077
H89B	1	1.2779	0.4326	0.8983	0.077
C90	1	1.2558 (4)	0.4974 (4)	0.9471 (3)	0.0694 (17)
H90A	1	1.2087	0.5042	0.9775	0.083
H90B	1	1.2644	0.5433	0.9042	0.083
C91	1	1.3367 (5)	0.4797 (5)	0.9840 (4)	0.087 (2)
H91A	1	1.3258	0.4370	1.0295	0.104
H91B	1	1.3822	0.4673	0.9562	0.104
C92	1	1.3670 (7)	0.5408 (6)	0.9950 (5)	0.126 (4)
H92A	1	1.3823	0.5821	0.9500	0.189
H92B	1	1.4162	0.5249	1.0204	0.189
H92C	1	1.3220	0.5543	1.0215	0.189
N9	1	1.0788 (2)	0.44220 (18)	0.57200 (18)	0.0292 (8)
N10	1	1.1471 (2)	0.54237 (18)	0.57584 (18)	0.0301 (8)
N11	1	1.0421 (2)	0.59086 (18)	0.49156 (18)	0.0296 (8)
N12	1	0.9561 (2)	0.68014 (18)	0.40457 (18)	0.0315 (8)
C93	1	1.0853 (3)	0.3673 (2)	0.6050 (2)	0.0308 (9)
C94	1	1.1495 (3)	0.3482 (2)	0.6530 (2)	0.0303 (9)
C95	1	1.1813 (3)	0.2804 (2)	0.6990 (2)	0.0320 (10)
H95	1	1.1600	0.2368	0.7044	0.038
C96	1	1.2466 (3)	0.2814 (2)	0.7365 (2)	0.0326 (10)
C97	1	1.2965 (3)	0.2171 (3)	0.7861 (2)	0.0413 (11)
H97A	1	1.3346	0.1969	0.7601	0.050
H97B	1	1.2578	0.1789	0.8207	0.050
C98	1	1.3484 (3)	0.2488 (3)	0.8224 (3)	0.0417 (11)
C99	1	1.3540 (3)	0.3322 (3)	0.7696 (3)	0.0419 (11)
H99A	1	1.3500	0.3611	0.7948	0.050
H99B	1	1.4077	0.3436	0.7387	0.050
C100	1	1.2794 (3)	0.3475 (2)	0.7280 (2)	0.0325 (10)
C101	1	1.2462 (3)	0.4145 (2)	0.6838 (2)	0.0301 (9)
H101	1	1.2663	0.4582	0.6792	0.036
C102	1	1.1813 (3)	0.4130 (2)	0.6467 (2)	0.0292 (9)
C103	1	1.1345 (3)	0.4732 (2)	0.5948 (2)	0.0286 (9)
C104	1	1.1026 (3)	0.5961 (2)	0.5283 (2)	0.0285 (9)
C105	1	1.1165 (3)	0.6726 (2)	0.5103 (2)	0.0374 (10)
C106	1	1.1716 (3)	0.7059 (3)	0.5327 (3)	0.0430 (12)
H106	1	1.2096	0.6786	0.5650	0.052
C107	1	1.1675 (4)	0.7808 (3)	0.5051 (3)	0.0493 (13)
C108	1	1.2196 (4)	0.8317 (3)	0.5181 (3)	0.0586 (15)
H10A	1	1.2760	0.8402	0.4913	0.070
H10B	1	1.2262	0.8118	0.5678	0.070
C109	1	1.1668 (4)	0.9030 (3)	0.4930 (4)	0.0637 (16)
C110	1	1.1203 (5)	0.9028 (3)	0.4336 (4)	0.0700 (19)
H11A	1	1.0653	0.9274	0.4307	0.084
H11B	1	1.1550	0.9267	0.3882	0.084
C111	1	1.1089 (4)	0.8227 (3)	0.4558 (3)	0.0505 (13)
C112	1	1.0548 (3)	0.7898 (2)	0.4335 (3)	0.0463 (12)
H112	1	1.0166	0.8172	0.4014	0.056
C113	1	1.0596 (3)	0.7132 (3)	0.4609 (2)	0.0389 (11)
C114	1	1.0146 (3)	0.6598 (2)	0.4504 (2)	0.0307 (9)
C115	1	1.2966 (4)	0.2407 (3)	0.8916 (3)	0.0556 (14)
H11C	1	1.3237	0.2705	0.9075	0.067
H11D	1	1.2396	0.2604	0.8815	0.067
C116	1	1.2875 (4)	0.1636 (4)	0.9516 (3)	0.077 (2)
H11E	1	1.2720	0.1310	0.9338	0.093
H11F	1	1.3423	0.1475	0.9699	0.093
C117	1	1.2203 (6)	0.1589 (6)	1.0106 (4)	0.121 (4)
H11G	1	1.2243	0.1099	1.0489	0.145
H11H	1	1.2389	0.1918	1.0269	0.145
C18A	0.677 (18)	1.1291 (8)	0.1732 (8)	1.0043 (9)	0.109 (5)
H11I	0.677 (18)	1.1213	0.2185	0.9622	0.131
H11J	0.677 (18)	1.1009	0.1779	1.0449	0.131
C19A	0.677 (18)	1.0902 (11)	0.1101 (9)	0.9998 (10)	0.138 (7)
H11K	0.677 (18)	1.0970	0.0661	1.0433	0.166

H11L	0.677 (18)	1.1237	0.1036	0.9618	0.166
C20A	0.677 (18)	0.9957 (11)	0.1161 (11)	0.9876 (12)	0.146 (7)
H12A	0.677 (18)	0.9602	0.1047	1.0312	0.219
H12B	0.677 (18)	0.9839	0.0823	0.9706	0.219
H12C	0.677 (18)	0.9838	0.1650	0.9534	0.219
C18B	0.323 (18)	1.1362 (11)	0.1468 (15)	0.9855 (11)	0.076 (7)
H11I	0.323 (18)	1.1261	0.1894	0.9418	0.091
H11J	0.323 (18)	1.1441	0.1051	0.9760	0.091
C19B	0.323 (18)	1.0587 (13)	0.1339 (16)	1.0390 (13)	0.102 (10)
H11K	0.323 (18)	1.0693	0.0906	1.0820	0.122
H11L	0.323 (18)	1.0535	0.1749	1.0497	0.122
C20B	0.323 (18)	0.9747 (17)	0.1244 (17)	1.0193 (18)	0.104 (10)
H12A	0.323 (18)	0.9664	0.0736	1.0328	0.156
H12B	0.323 (18)	0.9743	0.1526	0.9692	0.156
H12C	0.323 (18)	0.9293	0.1407	1.0432	0.156
C121	1	1.4384 (4)	0.2144 (3)	0.8313 (4)	0.0660 (17)
H12D	1	1.4316	0.1623	0.8621	0.079
H12E	1	1.4646	0.2203	0.7856	0.079
C122	1	1.4983 (4)	0.2425 (4)	0.8594 (4)	0.078 (2)
H12F	1	1.4829	0.2226	0.9100	0.093
H12G	1	1.4921	0.2952	0.8390	0.093
C123	1	1.5946 (5)	0.2237 (5)	0.8448 (4)	0.094 (3)
H12H	1	1.5998	0.1715	0.8605	0.113
H12I	1	1.6120	0.2483	0.7943	0.113
C124	1	1.6536 (5)	0.2454 (4)	0.8804 (5)	0.093 (3)
H12J	1	1.6434	0.2964	0.8690	0.112
H12K	1	1.6402	0.2166	0.9311	0.112
C125	1	1.7445 (5)	0.2361 (5)	0.8612 (4)	0.109 (3)
H12L	1	1.7579	0.2631	0.8104	0.130
H12M	1	1.7560	0.1848	0.8750	0.130
C126	1	1.8006 (7)	0.2622 (7)	0.8957 (5)	0.141 (4)
H12N	1	1.7900	0.3132	0.8815	0.211
H12O	1	1.8597	0.2554	0.8818	0.211
H12P	1	1.7883	0.2349	0.9460	0.211
C127	1	1.2252 (5)	0.9709 (3)	0.4649 (4)	0.0744 (19)
H12Q	1	1.2550	0.9668	0.5032	0.089
H12R	1	1.2682	0.9696	0.4287	0.089
C128	1	1.1816 (5)	1.0443 (3)	0.4344 (5)	0.094 (3)
H12S	1	1.1389	1.0464	0.4704	0.113
H12T	1	1.1519	1.0490	0.3959	0.113
C129	1	1.2423 (6)	1.1085 (4)	0.4075 (5)	0.099 (3)
H12U	1	1.2880	1.1034	0.3750	0.119
H12V	1	1.2682	1.1056	0.4471	0.119
C130	1	1.2027 (6)	1.1843 (4)	0.3703 (6)	0.113 (3)
H13A	1	1.2470	1.2209	0.3557	0.136
H13B	1	1.1809	1.1892	0.3282	0.136
C131	1	1.1352 (7)	1.1980 (5)	0.4132 (5)	0.104 (3)
H13C	1	1.1555	1.1886	0.4572	0.125
H13D	1	1.0886	1.1642	0.4243	0.125
C132	1	1.0997 (7)	1.2783 (4)	0.3776 (5)	0.114 (3)
H13E	1	1.1468	1.3119	0.3545	0.172
H13F	1	1.0678	1.2890	0.4130	0.172
H13G	1	1.0629	1.2831	0.3435	0.172
C133	1	1.1004 (5)	0.8988 (4)	0.5532 (4)	0.081 (2)
H13H	1	1.0688	0.8533	0.5723	0.098
H13I	1	1.0599	0.9386	0.5344	0.098
C134	1	1.1386 (8)	0.9028 (6)	0.6141 (5)	0.119 (3)
H13J	1	1.1942	0.8791	0.6176	0.143
H13K	1	1.1491	0.9540	0.5992	0.143
C135	1	1.0954 (13)	0.8739 (11)	0.6825 (11)	0.262 (11)
H13L	1	1.1335	0.8734	0.7147	0.314
H13M	1	1.0782	0.8240	0.6977	0.314
C36A	0.56 (2)	1.0194 (14)	0.9182 (14)	0.6845 (12)	0.135 (8)
H13N	0.56 (2)	0.9812	0.9155	0.6540	0.162
H13O	0.56 (2)	1.0377	0.9687	0.6641	0.162

C37A	0.56 (2)	0.967 (2)	0.899 (3)	0.7563 (18)	0.27 (2)
H13P	0.56 (2)	1.0094	0.8779	0.7893	0.325
H13Q	0.56 (2)	0.9537	0.9465	0.7543	0.325
C38A	0.56 (2)	0.8890 (14)	0.8556 (15)	0.7956 (12)	0.171 (11)
H13R	0.56 (2)	0.8393	0.8829	0.7759	0.256
H13S	0.56 (2)	0.8856	0.8449	0.8443	0.256
H13T	0.56 (2)	0.8915	0.8107	0.7922	0.256
C36B	0.44 (2)	1.0082 (15)	0.8629 (17)	0.6976 (14)	0.175 (14)
H13N	0.44 (2)	0.9942	0.8202	0.6931	0.210
H13O	0.44 (2)	0.9796	0.9048	0.6634	0.210
C37B	0.44 (2)	0.9741 (18)	0.8516 (17)	0.7732 (13)	0.138 (11)
H13P	0.44 (2)	0.9526	0.8021	0.8013	0.166
H13Q	0.44 (2)	1.0212	0.8575	0.7951	0.166
C38B	0.44 (2)	0.9056 (19)	0.9031 (19)	0.7732 (18)	0.143 (11)
H13R	0.44 (2)	0.9292	0.9514	0.7537	0.214
H13S	0.44 (2)	0.8798	0.8886	0.8207	0.214
H13T	0.44 (2)	0.8629	0.9031	0.7452	0.214

Table S2. *Anisotropic displacement parameters* (Å^2)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N1	0.0239 (17)	0.0223 (16)	0.0230 (17)	−0.0004 (13)	−0.0002 (14)	−0.0095 (14)
N2	0.0236 (17)	0.0242 (17)	0.0243 (17)	−0.0019 (13)	−0.0010 (14)	−0.0075 (14)
N3	0.0265 (17)	0.0212 (17)	0.0279 (18)	0.0009 (13)	−0.0059 (14)	−0.0090 (14)
N4	0.0324 (19)	0.0248 (18)	0.0323 (19)	0.0015 (14)	−0.0082 (16)	−0.0125 (15)
N5	0.0291 (18)	0.0208 (17)	0.0289 (18)	0.0016 (14)	−0.0050 (15)	−0.0048 (14)
N6	0.0292 (19)	0.036 (2)	0.036 (2)	0.0002 (16)	−0.0101 (16)	−0.0092 (17)
N7	0.0266 (18)	0.0279 (18)	0.0215 (17)	−0.0005 (14)	−0.0013 (14)	−0.0071 (14)
N8	0.0270 (18)	0.0317 (19)	0.0246 (17)	−0.0033 (14)	−0.0025 (14)	−0.0143 (15)
C1	0.028 (2)	0.0193 (19)	0.025 (2)	−0.0027 (16)	0.0057 (17)	−0.0104 (16)
C2	0.026 (2)	0.040 (2)	0.023 (2)	0.0053 (18)	0.0007 (17)	−0.0185 (18)
C3	0.037 (2)	0.026 (2)	0.047 (3)	−0.0028 (18)	−0.012 (2)	−0.021 (2)
C4	0.042 (3)	0.033 (2)	0.053 (3)	−0.005 (2)	−0.008 (2)	−0.025 (2)
C5	0.059 (3)	0.029 (3)	0.080 (4)	0.003 (2)	−0.025 (3)	−0.027 (3)
C6	0.062 (3)	0.026 (3)	0.079 (4)	0.002 (2)	−0.023 (3)	−0.018 (3)
C7	0.054 (3)	0.018 (2)	0.074 (4)	0.002 (2)	−0.022 (3)	−0.017 (2)
C8	0.038 (3)	0.028 (2)	0.049 (3)	0.0065 (19)	−0.010 (2)	−0.018 (2)
C9	0.031 (2)	0.023 (2)	0.032 (2)	0.0014 (17)	−0.0073 (18)	−0.0104 (18)
C10	0.027 (2)	0.033 (2)	0.026 (2)	−0.0016 (17)	0.0032 (17)	−0.0165 (18)
C11	0.027 (2)	0.0198 (19)	0.0153 (18)	0.0024 (15)	0.0088 (15)	−0.0072 (15)
C12	0.025 (2)	0.029 (2)	0.022 (2)	0.0011 (17)	−0.0031 (16)	−0.0095 (17)
C13	0.026 (2)	0.028 (2)	0.022 (2)	−0.0007 (16)	−0.0009 (16)	−0.0087 (17)
C14	0.029 (3)	0.022 (2)	0.024 (2)	−0.0003 (16)	−0.0022 (17)	−0.0082 (16)
C15	0.028 (2)	0.034 (2)	0.020 (2)	−0.0034 (18)	0.0005 (17)	−0.0090 (18)
C16	0.035 (2)	0.041 (3)	0.022 (2)	−0.0025 (19)	−0.0036 (18)	−0.0119 (19)
C17	0.033 (2)	0.047 (3)	0.028 (2)	−0.001 (2)	−0.0073 (19)	−0.018 (2)
C18	0.029 (2)	0.038 (2)	0.030 (2)	−0.0021 (18)	−0.0044 (18)	−0.0193 (19)
C19	0.030 (2)	0.035 (2)	0.021 (2)	−0.0030 (18)	−0.0016 (17)	−0.0125 (18)
C20	0.034 (2)	0.0210 (19)	0.025 (2)	−0.0003 (17)	−0.0005 (17)	−0.0122 (17)
C21	0.029 (2)	0.022 (2)	0.022 (2)	−0.0007 (16)	0.0046 (16)	−0.0110 (16)
C22	0.025 (2)	0.026 (2)	0.029 (2)	−0.0011 (16)	−0.0008 (17)	−0.0144 (17)
C23	0.030 (2)	0.023 (2)	0.037 (2)	−0.0018 (17)	−0.0013 (19)	−0.0110 (18)
C24	0.037 (3)	0.029 (2)	0.044 (3)	0.0065 (19)	−0.015 (2)	−0.006 (2)
C25	0.048 (3)	0.023 (2)	0.062 (3)	0.000 (2)	−0.021 (3)	−0.007 (2)
C26	0.057 (3)	0.025 (2)	0.074 (4)	0.003 (2)	−0.022 (3)	−0.011 (2)
C27	0.078 (4)	0.027 (3)	0.091 (5)	−0.002 (3)	−0.034 (4)	−0.005 (3)
C28	0.075 (4)	0.031 (3)	0.093 (5)	−0.004 (3)	−0.032 (4)	0.008 (3)
C29	0.085 (5)	0.030 (3)	0.100 (5)	0.006 (3)	−0.046 (4)	0.001 (3)
C30	0.060 (4)	0.030 (3)	0.075 (4)	0.005 (2)	−0.031 (3)	−0.001 (3)
C31	0.053 (3)	0.028 (3)	0.071 (4)	−0.001 (2)	−0.035 (3)	−0.001 (2)
C32	0.040 (3)	0.032 (2)	0.049 (3)	0.003 (2)	−0.013 (2)	−0.010 (2)
C33	0.034 (2)	0.029 (2)	0.034 (2)	0.0043 (18)	−0.0095 (19)	−0.0072 (19)
C34	0.027 (2)	0.039 (2)	0.020 (2)	0.0012 (18)	−0.0009 (17)	−0.0112 (18)
C35	0.024 (2)	0.036 (2)	0.032 (2)	−0.0005 (18)	−0.0063 (18)	−0.0099 (19)
C36	0.028 (2)	0.038 (2)	0.025 (2)	0.0024 (18)	−0.0038 (18)	−0.0072 (19)

C37	0.027 (2)	0.053 (3)	0.022 (2)	0.001 (2)	−0.0001 (17)	−0.015 (2)
C38	0.033 (2)	0.056 (3)	0.033 (2)	0.008 (2)	−0.009 (2)	−0.020 (2)
C39	0.031 (2)	0.059 (3)	0.040 (3)	0.008 (2)	−0.010 (2)	−0.026 (2)
C40	0.034 (3)	0.048 (3)	0.047 (3)	0.004 (2)	−0.010 (2)	−0.028 (2)
C41	0.027 (2)	0.056 (3)	0.032 (2)	−0.001 (2)	−0.0049 (19)	−0.024 (2)
C42	0.028 (2)	0.039 (2)	0.029 (2)	−0.0031 (18)	0.0025 (18)	−0.0188 (19)
C43	0.026 (2)	0.045 (3)	0.025 (2)	0.0017 (19)	0.0029 (17)	−0.018 (2)
C44	0.025 (2)	0.034 (2)	0.030 (2)	−0.0021 (17)	−0.0051 (17)	−0.0139 (19)
C45	0.072 (4)	0.035 (3)	0.107 (6)	−0.004 (3)	−0.016 (4)	−0.029 (3)
C46	0.085 (5)	0.057 (4)	0.092 (5)	−0.014 (3)	−0.002 (4)	−0.028 (4)
C47	0.085 (5)	0.057 (4)	0.138 (7)	−0.006 (4)	0.003 (5)	−0.051 (5)
C48	0.095 (6)	0.056 (4)	0.164 (9)	0.010 (4)	−0.005 (6)	−0.055 (5)
C50	0.199 (12)	0.082 (7)	0.176 (11)	−0.062 (7)	0.059 (10)	−0.062 (7)
C51	0.070 (4)	0.057 (4)	0.071 (4)	−0.018 (3)	−0.017 (3)	−0.014 (3)
C53	0.084 (5)	0.100 (6)	0.114 (7)	−0.008 (5)	−0.012 (5)	−0.035 (5)
C56	0.30 (3)	0.70 (6)	0.28 (3)	0.34 (4)	−0.07 (2)	−0.17 (4)
C57	0.039 (3)	0.051 (3)	0.035 (3)	0.002 (2)	−0.014 (2)	−0.019 (2)
C58	0.043 (3)	0.061 (3)	0.041 (3)	0.002 (2)	−0.010 (2)	−0.030 (3)
C59	0.046 (3)	0.063 (3)	0.050 (3)	0.004 (3)	−0.015 (2)	−0.032 (3)
C60	0.062 (4)	0.078 (4)	0.070 (4)	−0.003 (3)	−0.016 (3)	−0.048 (4)
C61	0.078 (5)	0.107 (6)	0.085 (5)	−0.021 (4)	−0.015 (4)	−0.058 (5)
C62	0.076 (5)	0.116 (7)	0.160 (9)	0.005 (5)	−0.029 (6)	−0.096 (7)
C63	0.041 (3)	0.068 (3)	0.030 (3)	−0.002 (2)	−0.001 (2)	−0.021 (2)
C64	0.062 (4)	0.109 (6)	0.042 (3)	−0.009 (4)	0.009 (3)	−0.034 (4)
C65	0.057 (4)	0.147 (8)	0.059 (4)	0.021 (4)	−0.003 (3)	−0.045 (5)
C69	0.118 (6)	0.027 (3)	0.122 (7)	0.003 (3)	−0.051 (5)	0.000 (3)
C70	0.158 (9)	0.038 (4)	0.186 (11)	−0.008 (5)	−0.049 (8)	−0.001 (5)
C71	0.189 (12)	0.063 (6)	0.173 (12)	0.009 (6)	−0.023 (9)	−0.026 (7)
C72	0.243 (15)	0.059 (6)	0.178 (12)	0.060 (7)	0.069 (11)	0.022 (7)
C74	0.30 (2)	0.161 (13)	0.171 (15)	−0.041 (13)	0.060 (14)	−0.071 (12)
C75	0.104 (6)	0.042 (4)	0.098 (6)	−0.013 (4)	−0.042 (5)	0.009 (4)
C76	0.138 (9)	0.088 (7)	0.134 (9)	−0.012 (6)	−0.044 (8)	−0.008 (6)
C77	0.169 (12)	0.112 (8)	0.121 (9)	−0.001 (8)	−0.011 (9)	−0.033 (7)
C78	0.092 (8)	0.175 (12)	0.157 (11)	0.016 (7)	−0.009 (7)	−0.068 (9)
C79	0.161 (13)	0.099 (9)	0.260 (19)	0.023 (9)	−0.024 (14)	0.018 (10)
C80	0.117 (10)	0.176 (14)	0.210 (15)	0.021 (9)	−0.029 (10)	−0.026 (11)
C81	0.044 (3)	0.058 (3)	0.043 (3)	0.013 (2)	−0.013 (2)	−0.025 (3)
C82	0.063 (4)	0.067 (4)	0.043 (3)	0.010 (3)	−0.006 (3)	−0.023 (3)
C83	0.082 (5)	0.095 (5)	0.045 (4)	0.002 (4)	0.007 (3)	−0.025 (4)
C84	0.102 (6)	0.092 (5)	0.060 (4)	−0.004 (4)	0.019 (4)	−0.031 (4)
C85	0.165 (10)	0.153 (10)	0.090 (7)	−0.021 (8)	0.067 (7)	−0.021 (7)
C86	0.209 (14)	0.123 (10)	0.176 (13)	0.015 (9)	0.099 (11)	0.016 (9)
C87	0.038 (3)	0.067 (4)	0.047 (3)	0.011 (2)	−0.013 (2)	−0.033 (3)
C88	0.045 (3)	0.076 (4)	0.049 (3)	0.007 (3)	−0.009 (2)	−0.038 (3)
C89	0.056 (4)	0.088 (5)	0.055 (4)	−0.002 (3)	−0.012 (3)	−0.037 (3)
C90	0.072 (4)	0.083 (5)	0.055 (4)	−0.006 (3)	−0.011 (3)	−0.033 (3)
C91	0.073 (5)	0.138 (7)	0.055 (4)	−0.016 (4)	−0.011 (3)	−0.047 (4)
C92	0.150 (9)	0.149 (9)	0.087 (6)	−0.061 (7)	−0.034 (6)	−0.049 (6)
N9	0.0343 (19)	0.0227 (17)	0.0286 (19)	0.0030 (15)	0.0000 (15)	−0.0114 (15)
N10	0.036 (2)	0.0261 (19)	0.0251 (18)	0.0050 (15)	−0.0043 (15)	−0.0094 (15)
N11	0.035 (2)	0.0225 (17)	0.0292 (19)	0.0075 (14)	−0.0083 (16)	−0.0101 (15)
N12	0.039 (2)	0.0252 (18)	0.0302 (19)	0.0069 (15)	−0.0087 (16)	−0.0124 (15)
C93	0.033 (2)	0.032 (2)	0.024 (2)	0.0082 (18)	−0.0007 (18)	−0.0117 (18)
C94	0.032 (2)	0.027 (2)	0.028 (2)	0.0046 (17)	0.0015 (18)	−0.0125 (18)
C95	0.042 (3)	0.0164 (19)	0.032 (2)	0.0049 (17)	−0.0057 (19)	−0.0063 (17)
C96	0.035 (2)	0.035 (2)	0.023 (2)	0.0095 (19)	−0.0007 (18)	−0.0109 (18)
C97	0.046 (3)	0.036 (3)	0.032 (2)	0.009 (2)	−0.010 (2)	−0.006 (2)
C98	0.037 (3)	0.037 (3)	0.039 (3)	0.007 (2)	−0.010 (2)	−0.007 (2)
C99	0.036 (3)	0.038 (3)	0.041 (3)	0.001 (2)	−0.009 (2)	−0.008 (2)
C100	0.027 (2)	0.039 (2)	0.027 (2)	−0.0024 (18)	0.0004 (17)	−0.0116 (19)
C101	0.030 (2)	0.027 (2)	0.028 (2)	0.0002 (17)	0.0028 (18)	−0.0100 (18)
C102	0.027 (2)	0.035 (2)	0.0164 (19)	0.0057 (18)	0.0045 (16)	−0.0067 (17)
C103	0.032 (2)	0.035 (2)	0.0181 (19)	0.0051 (18)	−0.0001 (17)	−0.0126 (18)
C104	0.040 (2)	0.0185 (19)	0.027 (2)	0.0024 (17)	0.0022 (18)	−0.0121 (17)
C105	0.045 (3)	0.028 (2)	0.037 (2)	0.007 (2)	−0.007 (2)	−0.013 (2)

C106	0.050 (3)	0.035 (3)	0.049 (3)	0.001 (2)	−0.018 (2)	−0.020 (2)
C107	0.062 (3)	0.039 (3)	0.049 (3)	0.003 (2)	−0.018 (3)	−0.020 (2)
C108	0.073 (4)	0.041 (3)	0.067 (4)	−0.005 (3)	−0.021 (3)	−0.025 (3)
C109	0.082 (4)	0.040 (3)	0.075 (4)	0.004 (3)	−0.025 (4)	−0.027 (3)
C110	0.093 (5)	0.031 (3)	0.087 (5)	0.004 (3)	−0.041 (4)	−0.021 (3)
C111	0.074 (4)	0.026 (2)	0.053 (3)	0.002 (2)	−0.021 (3)	−0.017 (2)
C112	0.062 (3)	0.026 (2)	0.051 (3)	0.008 (2)	−0.023 (3)	−0.015 (2)
C113	0.046 (3)	0.036 (2)	0.032 (2)	0.009 (2)	−0.009 (2)	−0.014 (2)
C114	0.042 (2)	0.0173 (19)	0.035 (2)	−0.0001 (17)	−0.001 (2)	−0.0156 (18)
C115	0.062 (4)	0.053 (3)	0.043 (3)	0.003 (3)	−0.013 (3)	−0.014 (3)
C116	0.079 (5)	0.066 (4)	0.051 (4)	0.004 (3)	−0.019 (3)	0.005 (3)
C117	0.102 (7)	0.130 (8)	0.066 (5)	−0.007 (6)	0.003 (5)	0.008 (5)
C121	0.056 (3)	0.047 (3)	0.085 (5)	0.007 (3)	−0.031 (3)	−0.016 (3)
C122	0.068 (4)	0.072 (4)	0.080 (5)	0.012 (3)	−0.029 (4)	−0.020 (4)
C123	0.068 (5)	0.108 (6)	0.077 (5)	0.027 (4)	−0.031 (4)	−0.015 (4)
C124	0.077 (5)	0.066 (5)	0.104 (6)	−0.006 (4)	−0.031 (4)	−0.005 (4)
C125	0.057 (4)	0.141 (8)	0.064 (5)	0.003 (5)	0.000 (4)	0.005 (5)
C126	0.121 (8)	0.189 (11)	0.095 (7)	−0.073 (8)	0.001 (6)	−0.046 (7)
C127	0.095 (5)	0.042 (3)	0.089 (5)	−0.010 (3)	−0.030 (4)	−0.027 (3)
C128	0.115 (6)	0.043 (4)	0.127 (7)	−0.005 (4)	−0.047 (5)	−0.032 (4)
C129	0.146 (8)	0.048 (4)	0.103 (6)	−0.019 (4)	−0.018 (5)	−0.031 (4)
C130	0.136 (8)	0.055 (5)	0.133 (8)	−0.031 (5)	0.009 (7)	−0.033 (5)
C131	0.140 (8)	0.087 (6)	0.092 (6)	−0.018 (5)	0.000 (6)	−0.048 (5)
C132	0.150 (8)	0.066 (5)	0.125 (8)	−0.001 (5)	−0.002 (6)	−0.045 (5)
C133	0.097 (5)	0.060 (4)	0.099 (6)	−0.006 (4)	−0.019 (5)	−0.044 (4)
C134	0.179 (10)	0.113 (7)	0.081 (6)	−0.005 (7)	−0.003 (7)	−0.061 (6)
C135	0.35 (3)	0.23 (2)	0.24 (2)	−0.10 (2)	−0.08 (2)	−0.113 (18)

Table 53. *Geometric parameters (Å, °)*

N1—C11	1.365 (5)	C14—C15	1.390 (6)
N1—C1	1.367 (5)	C15—C19	1.404 (6)
N2—C12	1.312 (5)	C15—C16	1.514 (6)
N2—C11	1.346 (5)	C16—C17	1.560 (5)
N3—C22	1.360 (5)	C17—C18	1.542 (5)
N3—C12	1.384 (5)	C17—C63	1.547 (6)
N4—C22	1.326 (5)	C17—C57	1.549 (5)
N4—C23	1.336 (5)	C18—C19	1.514 (6)
N5—C23	1.362 (5)	C19—C20	1.384 (6)
N5—C33	1.382 (5)	C20—C21	1.400 (6)
N6—C33	1.318 (6)	C21—C22	1.437 (6)
N6—C34	1.331 (6)	C23—C24	1.461 (6)
N7—C44	1.366 (5)	C24—C32	1.388 (7)
N7—C34	1.374 (5)	C24—C25	1.403 (7)
N8—C44	1.332 (5)	C25—C26	1.389 (7)
N8—C1	1.337 (5)	C26—C30	1.403 (8)
C1—C2	1.470 (6)	C26—C27	1.522 (7)
C2—C3	1.378 (6)	C27—C28	1.532 (9)
C2—C10	1.404 (6)	C28—C75	1.536 (11)
C3—C4	1.388 (6)	C28—C29	1.538 (9)
C4—C8	1.416 (7)	C28—C69	1.560 (9)
C4—C5	1.513 (6)	C29—C30	1.517 (7)
C5—C6	1.578 (8)	C30—C31	1.365 (8)
C6—C45	1.540 (7)	C31—C32	1.405 (6)
C6—C51	1.555 (9)	C32—C33	1.459 (6)
C6—C7	1.557 (7)	C34—C35	1.441 (6)
C7—C8	1.515 (6)	C35—C43	1.394 (6)
C8—C9	1.381 (6)	C35—C36	1.401 (6)
C9—C10	1.403 (6)	C36—C37	1.382 (6)
C10—C11	1.447 (6)	C37—C41	1.408 (7)
C12—C13	1.464 (6)	C37—C38	1.500 (6)
C13—C14	1.399 (6)	C38—C39	1.537 (7)
C13—C21	1.404 (5)	C39—C81	1.546 (7)

C39—C87	1.550 (6)	N10—C104	1.345 (5)
C39—C40	1.563 (7)	N11—C104	1.355 (6)
C40—C41	1.508 (6)	N11—C114	1.363 (5)
C41—C42	1.398 (6)	N12—C93^{i}	1.313 (6)
C42—C43	1.395 (6)	N12—C114	1.343 (6)
C43—C44	1.468 (6)	C93—N12^{i}	1.313 (6)
C45—C46	1.452 (10)	C93—C94	1.447 (6)
C46—C47	1.576 (9)	C94—C102	1.396 (6)
C47—C48	1.438 (11)	C94—C95	1.398 (6)
C48—C49A	1.492 (14)	C95—C96	1.394 (6)
C48—C49B	1.568 (13)	C96—C100	1.411 (6)
C49A—C50	1.454 (15)	C96—C97	1.516 (6)
C49B—C50	1.481 (13)	C97—C98	1.553 (7)
C51—C52	1.501 (10)	C98—C121	1.538 (7)
C52—C53B	1.478 (16)	C98—C115	1.543 (7)
C52—C53A	1.558 (12)	C98—C99	1.563 (6)
C53A—C54A	1.534 (13)	C99—C100	1.501 (6)
C54A—C55A	1.536 (14)	C100—C101	1.384 (6)
C55A—C56	1.452 (17)	C101—C102	1.387 (6)
C53B—C54B	1.513 (17)	C102—C103	1.467 (6)
C54B—C55B	1.538 (18)	C104—C105	1.463 (6)
C55B—C56	1.501 (19)	C105—C106	1.396 (7)
C57—C58	1.514 (7)	C105—C113	1.404 (6)
C58—C59	1.523 (7)	C106—C107	1.375 (7)
C59—C60	1.526 (8)	C107—C111	1.427 (7)
C60—C61	1.526 (8)	C107—C108	1.515 (7)
C61—C62	1.476 (10)	C108—C109	1.542 (8)
C63—C64	1.533 (8)	C109—C133	1.524 (10)
C64—C65	1.520 (10)	C109—C127	1.547 (8)
C65—C66B	1.464 (14)	C109—C110	1.557 (8)
C65—C66A	1.603 (11)	C110—C111	1.510 (7)
C66A—C67A	1.509 (14)	C111—C112	1.376 (7)
C67A—C68A	1.518 (16)	C112—C113	1.408 (6)
C66B—C67B	1.487 (17)	C113—C114	1.461 (6)
C67B—C68B	1.513 (18)	C115—C116	1.515 (8)
C69—C70	1.485 (12)	C116—C117	1.512 (11)
C70—C71	1.574 (12)	C117—C18A	1.458 (13)
C71—C72	1.520 (17)	C117—C18B	1.568 (16)
C72—C73B	1.638 (18)	C18A—C19A	1.518 (16)
C72—C73A	1.77 (5)	C19A—C20A	1.532 (15)
C73A—C74	1.498 (19)	C18B—C19B	1.504 (18)
C73B—C74	1.516 (14)	C19B—C20B	1.491 (18)
C75—C76	1.455 (12)	C121—C122	1.460 (9)
C76—C77	1.506 (15)	C122—C123	1.568 (10)
C77—C78	1.483 (15)	C123—C124	1.487 (11)
C78—C79	1.516 (14)	C124—C125	1.461 (10)
C79—C80	1.475 (13)	C125—C126	1.493 (12)
C81—C82	1.529 (7)	C127—C128	1.506 (9)
C82—C83	1.518 (8)	C128—C129	1.516 (10)
C83—C84	1.537 (10)	C129—C130	1.526 (11)
C84—C85	1.505 (12)	C130—C131	1.414 (12)
C85—C86	1.424 (14)	C131—C132	1.571 (11)
C87—C88	1.507 (7)	C133—C134	1.550 (11)
C88—C89	1.539 (7)	C134—C135	1.40 (2)
C89—C90	1.504 (9)	C135—C36B	1.375 (17)
C90—C91	1.525 (9)	C135—C36A	1.466 (16)
C91—C92	1.499 (11)	C36A—C37A	1.535 (18)
N9—C93	1.373 (5)	C37A—C38A	1.480 (18)
N9—C103	1.375 (5)	C36B—C37B	1.557 (18)
N10—C103	1.310 (5)	C37B—C38B	1.466 (18)
C11—N1—C1	107.9 (3)	C22—N3—C12	109.7 (3)
C12—N2—C11	123.2 (3)	C22—N4—C23	122.4 (4)

C23—N5—C33	107.9 (3)	N5—C23—C24	109.9 (4)
C33—N6—C34	123.5 (4)	C32—C24—C25	122.2 (4)
C44—N7—C34	110.1 (3)	C32—C24—C23	106.3 (4)
C44—N8—C1	122.0 (3)	C25—C24—C23	131.5 (4)
N8—C1—N1	128.5 (3)	C26—C25—C24	115.8 (5)
N8—C1—C2	121.6 (3)	C25—C26—C30	121.9 (5)
N1—C1—C2	109.9 (3)	C25—C26—C27	128.4 (5)
C3—C2—C10	122.1 (4)	C30—C26—C27	109.7 (5)
C3—C2—C1	132.7 (4)	C26—C27—C28	104.0 (5)
C10—C2—C1	105.1 (4)	C27—C28—C75	107.1 (6)
C2—C3—C4	116.9 (4)	C27—C28—C29	103.4 (5)
C3—C4—C8	121.2 (4)	C75—C28—C29	110.1 (7)
C3—C4—C5	129.3 (4)	C27—C28—C69	111.3 (7)
C8—C4—C5	109.6 (4)	C75—C28—C69	113.0 (6)
C4—C5—C6	104.6 (4)	C29—C28—C69	111.5 (6)
C45—C6—C51	110.7 (5)	C30—C29—C28	104.3 (5)
C45—C6—C7	113.3 (5)	C31—C30—C26	122.2 (5)
C51—C6—C7	108.0 (5)	C31—C30—C29	128.8 (5)
C45—C6—C5	113.9 (5)	C26—C30—C29	109.0 (5)
C51—C6—C5	108.6 (5)	C30—C31—C32	116.8 (5)
C7—C6—C5	101.9 (4)	C24—C32—C31	121.2 (4)
C8—C7—C6	104.8 (4)	C24—C32—C33	106.8 (4)
C9—C8—C4	122.1 (4)	C31—C32—C33	132.0 (5)
C9—C8—C7	128.2 (4)	N6—C33—N5	127.8 (4)
C4—C8—C7	109.8 (4)	N6—C33—C32	123.1 (4)
C8—C9—C10	116.3 (4)	N5—C33—C32	109.1 (4)
C9—C10—C2	121.3 (4)	N6—C34—N7	128.9 (4)
C9—C10—C11	131.7 (4)	N6—C34—C35	123.2 (4)
C2—C10—C11	106.9 (4)	N7—C34—C35	107.9 (4)
N2—C11—N1	128.3 (3)	C43—C35—C36	122.5 (4)
N2—C11—C10	121.7 (3)	C43—C35—C34	108.0 (4)
N1—C11—C10	110.0 (3)	C36—C35—C34	129.4 (4)
N2—C12—N3	127.7 (4)	C37—C36—C35	116.4 (4)
N2—C12—C13	124.7 (4)	C36—C37—C41	121.5 (4)
N3—C12—C13	107.5 (3)	C36—C37—C38	128.3 (4)
C14—C13—C21	122.1 (4)	C41—C37—C38	110.3 (4)
C14—C13—C12	131.5 (4)	C37—C38—C39	103.5 (4)
C21—C13—C12	106.4 (3)	C38—C39—C81	109.7 (4)
C15—C14—C13	115.8 (4)	C38—C39—C87	110.6 (4)
C14—C15—C19	122.4 (4)	C81—C39—C87	111.4 (4)
C14—C15—C16	128.3 (4)	C38—C39—C40	101.5 (4)
C19—C15—C16	109.1 (4)	C81—C39—C40	109.4 (4)
C15—C16—C17	103.8 (4)	C87—C39—C40	113.7 (4)
C18—C17—C63	112.5 (4)	C41—C40—C39	103.9 (4)
C18—C17—C57	111.1 (4)	C42—C41—C37	122.0 (4)
C63—C17—C57	109.5 (4)	C42—C41—C40	129.7 (4)
C18—C17—C16	102.6 (3)	C37—C41—C40	108.3 (4)
C63—C17—C16	109.8 (4)	C43—C42—C41	116.4 (4)
C57—C17—C16	111.3 (4)	C35—C43—C42	121.2 (4)
C19—C18—C17	103.5 (3)	C35—C43—C44	106.1 (4)
C20—C19—C15	121.5 (4)	C42—C43—C44	132.6 (4)
C20—C19—C18	128.2 (4)	N8—C44—N7	127.2 (4)
C15—C19—C18	110.1 (4)	N8—C44—C43	124.8 (4)
C19—C20—C21	116.9 (4)	N7—C44—C43	108.0 (4)
C20—C21—C13	121 2 (4)	C46—C45—C6	117.0 (6)
C20—C21—C22	131.6 (4)	C45—C46—C47	113.1 (6)
C13—C21—C22	107.2 (3)	C48—C47—C46	113.8 (7)
N4—C22—N3	128.1 (4)	C47—C48—C49A	122.0 (9)
N4—C22—C21	122.8 (4)	C47—C48—C49B	114.1 (8)
N3—C22—C21	109.1 (3)	C49A—C48—C49B	33.9 (8)
N4—C23—N5	127.5 (4)	C50—C49A—C48	112.5 (12)
N4—C23—C24	122.6 (4)	C50—C49B—C48	106.9 (10)

C49A—C50—C49B	35.5 (9)
C52—C51—C6	118.6 (6)
C53B—C52—C51	118.7 (12)
C53B—C52—C53A	33.3 (9)
C51—C52—C53A	110.7 (8)
C54A—C53A—C52	110.1 (9)
C53A—C54A—C55A	121.0 (10)
C56—C55A—C54A	104.1 (13)
C52—C53B—C54B	111.5 (16)
C53B—C54B—C55B	115 (2)
C56—C55B—C54B	111 (2)
C55A—C56—C55B	36.0 (14)
C58—C57—C17	115.5 (4)
C57—C58—C59	113.5 (4)
C58—C59—C60	114.6 (5)
C59—C60—C61	114.3 (5)
C62—C61—C60	114.6 (6)
C64—C63—C17	120.1 (4)
C65—C64—C63	116.3 (6)
C66B—C65—C64	129.6 (10)
C66B—C65—C66A	30.0 (7)
C64—C65—C66A	104.1 (7)
C67A—C66A—C65	109.4 (10)
C66A—C67A—C68A	112.8 (12)
C65—C66B—C67B	125.8 (15)
C66B—C67B—C68B	110.3 (17)
C70—C69—C28	116.6 (6)
C69—C70—C71	115.9 (9)
C72—C71—C70	109.0 (10)
C71—C72—C73B	108.8 (12)
C71—C72—C73A	148.9 (19)
C73B—C72—C73A	60.9 (13)
C74—C73A—C72	102 (3)
C74—C73B—C72	107.3 (12)
C73A—C74—C73B	70 (2)
C76—C75—C28	116.7 (8)
C75—C76—C77	112.1 (10)
C78—C77—C76	115.9 (11)
C77—C78—C79	113.4 (12)
C80—C79—C78	114.0 (14)
C82—C81—C39	117.1 (4)
C83—C82—C81	112.2 (5)
C82—C83—C84	114.5 (6)
C85—C84—C83	115.1 (7)
C86—C85—C84	116.9 (11)
C88—C87—C39	116.3 (4)
C87—C88—C89	111.7 (5)
C90—C89—C88	113.1 (5)
C89—C90—C91	114.3 (6)
C92—C91—C90	114.2 (8)
C93—N9—C103	111.1 (3)
C103—N10—C104	122.2 (4)
C104—N11—C114	107.8 (3)
C93^{i}—N12—C114	122.5 (4)
N12^{i}—C93—N9	128.2 (4)
N12^{i}—C93—C94	124.5 (4)
N9—C93—C94	107.2 (4)
C102—C94—C95	120.8 (4)
C102—C94—C93	107.9 (4)
C95—C94—C93	131.3 (4)
C96—C95—C94	116.7 (4)
C95—C96—C100	121.7 (4)
C95—C96—C97	128.1 (4)
C100—C96—C97	110.1 (4)
C96—C97—C98	105.1 (4)
C121—C98—C115	114.1 (4)
C121—C98—C97	110.5 (4)
C115—C98—C97	110.0 (4)
C121—C98—C99	110.8 (4)
C115—C98—C99	107.5 (4)
C97—C98—C99	103.4 (4)
C100—C99—C98	105.4 (4)
C101—C100—C96	121.5 (4)
C101—C100—C99	128.4 (4)
C96—C100—C99	110.0 (4)
C100—C101—C102	116.4 (4)
C101—C102—C94	122.9 (4)
C101—C102—C103	130.3 (4)
C94—C102—C103	106.8 (4)
N10—C103—N9	129.2 (4)
N10—C103—C102	123.9 (4)
N9—C103—C102	107.0 (4)
N10—C104—N11	128.9 (4)
N10—C104—C105	120.6 (4)
N11—C104—C105	110.5 (4)
C106—C105—C113	122.0 (4)
C106—C105—C104	132.4 (4)
C113—C105—C104	105.6 (4)
C107—C106—C105	117.3 (4)
C106—C107—C111	121.3 (5)
C106—C107—C108	129.3 (5)
C111—C107—C108	109.4 (4)
C107—C108—C109	104.1 (5)
C133—C109—C108	109.5 (5)
C133—C109—C127	111.3 (5)
C108—C109—C127	111.4 (5)
C133—C109—C110	109.4 (6)
C108—C109—C110	103.3 (5)
C127—C109—C110	111.6 (5)
C111—C110—C109	103.8 (4)
C112—C111—C107	121.4 (4)
C112—C111—C110	129.2 (5)
C107—C111—C110	109.4 (5)
C111—C112—C113	117.5 (4)
C105—C113—C112	120.5 (4)
C105—C113—C114	105.7 (4)
C112—C113—C114	133.7 (4)
N12—C114—N11	127.8 (4)
N12—C114—C113	121.9 (4)
N11—C114—C113	110.3 (4)
C116—C115—C98	115.9 (5)
C117—C116—C115	111.8 (6)
C18A—C117—C116	124.8 (10)
C18A—C117—C18B	30.7 (9)
C116—C117—C18B	101.9 (10)
C117—C18A—C19A	108.7 (12)
C18A—C19A—C20A	117.7 (14)
C19B—C18B—C117	112.9 (16)
C20B—C19B—C18B	117 (2)
C122—C121—C98	117.7 (6)
C121—C122—C123	114.1 (7)
C124—C123—C122	113.4 (7)
C125—C124—C123	114.2 (8)
C124—C125—C126	111.8 (9)

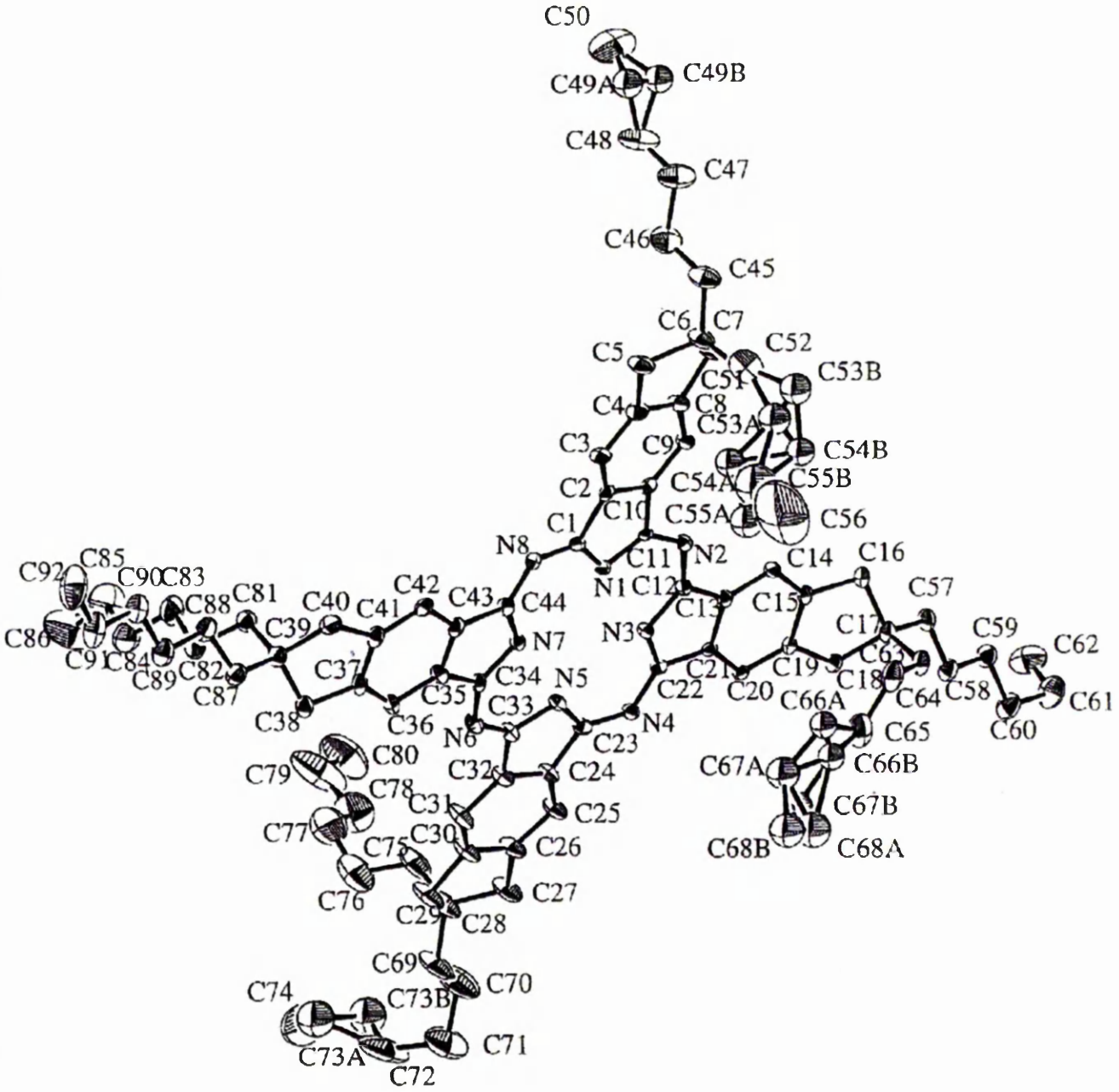
C128—C127—C109	116.5 (6)	C36B—C135—C134	123.5 (19)
C127—C128—C129	113.9 (7)	C36B—C135—C36A	43.7 (14)
C128—C129—C130	116.0 (8)	C134—C135—C36A	110.2 (19)
C131—C130—C129	113.2 (8)	C135—C36A—C37A	118 (3)
C130—C131—C132	113.4 (8)	C38A—C37A—C36A	135 (3)
C109—C133—C134	114.3 (7)	C135—C36B—C37B	112 (2)
C135—C134—C133	121.8 (11)	C38B—C37B—C36B	113 (2)
C44—N8—C1—N1	−1.1 (6)	C19—C15—C16—C17	−18.9 (4)
C44—N8—C1—C2	177.9 (4)	C15—C16—C17—C18	30.8 (4)
C11—N1—C1—N8	178.3 (4)	C15—C16—C17—C63	−88.9 (4)
C11—N1—C1—C2	−0.7 (4)	C15—C16—C17—C57	149.7 (4)
N8—C1—C2—C3	7.0 (7)	C63—C17—C18—C19	86.4 (4)
N1—C1—C2—C3	−173.8 (4)	C57—C17—C18—C19	−150.4 (4)
N8—C1—C2—C10	−176.8 (4)	C16—C17—C18—C19	−31.4 (4)
N1—C1—C2—C10	2.4 (4)	C14—C15—C19—C20	−1.0 (6)
C10—C2—C3—C4	2.2 (6)	C16—C15—C19—C20	175.2 (4)
C1—C2—C3—C4	177.9 (4)	C14—C15—C19—C18	−177.5 (4)
C2—C3—C4—C8	0.8 (7)	C16—C15—C19—C18	−1.3 (5)
C2—C3—C4—C5	179.9 (5)	C17—C18—C19—C20	−155.0 (4)
C3—C4—C5—C6	163.0 (5)	C17—C18—C19—C15	21.3 (5)
C8—C4—C5—C6	−17.8 (6)	C15—C19—C20—C21	−1.4 (6)
C4—C5—C6—C45	151.0 (5)	C18—C19—C20—C21	174.4 (4)
C4—C5—C6—C51	−85.2 (5)	C19—C20—C21—C13	1.7 (6)
C4—C5—C6—C7	28.6 (6)	C19—C20—C21—C22	−177.7 (4)
C45—C6—C7—C8	−152.0 (5)	C14—C13—C21—C20	0.3 (6)
C51—C6—C7—C8	85.0 (5)	C12—C13—C21—C20	−178.8 (4)
C5—C6—C7—C8	−29.2 (6)	C14—C13—C21—C22	179.8 (4)
C3—C4—C8—C9	−2.5 (8)	C12—C13—C21—C22	0.7 (4)
C5—C4—C8—C9	178.2 (5)	C23—N4—C22—N3	0.6 (7)
C3—C4—C8—C7	178.1 (5)	C23—N4—C22—C21	−176.5 (4)
C5—C4—C8—C7	−1.1 (8)	C12—N3—C22—N4	−174.5 (4)
C6—C7—C8—C9	−159.4 (5)	C12—N3—C22—C21	2.9 (4)
C6—C7—C8—C4	19.9 (6)	C20—C21—C22—N4	−5.2 (7)
C4—C8—C9—C10	1.2 (7)	C13—C21—C22—N4	175.3 (4)
C7—C8—C9—C10	−179.6 (5)	C20—C21—C22—N3	177.3 (4)
C8—C9—C10—C2	1.7 (6)	C13—C21—C22—N3	−2.2 (4)
C8—C9—C10—C11	−174.8 (4)	C22—N4—C23—N5	−6.2 (7)
C3—C2—C10—C9	−3.6 (6)	C22—N4—C23—C24	174.1 (4)
C1—C2—C10—C9	179.7 (4)	C33—N5—C23—N4	−179.0 (4)
C3—C2—C10—C11	173.7 (4)	C33—N5—C23—C24	0.7 (5)
C1—C2—C10—C11	−3.0 (4)	N4—C23—C24—C32	179.7 (4)
C12—N2—C11—N1	−0.3 (6)	N5—C23—C24—C32	−0.1 (5)
C12—N2—C11—C10	178.1 (4)	N4—C23—C24—C25	−3.6 (8)
C1—N1—C11—N2	177.3 (4)	N5—C23—C24—C25	176.7 (5)
C1—N1—C11—C10	−1.2 (4)	C32—C24—C25—C26	−0.6 (8)
C9—C10—C11—N2	1.0 (6)	C23—C24—C25—C26	−176.9 (5)
C2—C10—C11—N2	−175.9 (3)	C24—C25—C26—C30	0.4 (9)
C9—C10—C11—N1	179.6 (4)	C24—C25—C26—C27	179.3 (6)
C2—C10—C11—N1	2.7 (4)	C25—C26—C27—C28	−160.3 (7)
C11—N2—C12—N3	2.3 (6)	C30—C26—C27—C28	18.7 (8)
C11—N2—C12—C13	−177.0 (4)	C26—C27—C28—C75	87.0 (6)
C22—N3—C12—N2	178.2 (4)	C26—C27—C28—C29	−29.3 (7)
C22—N3—C12—C13	−2.4 (4)	C26—C27—C28—C69	−149.2 (6)
N2—C12—C13—C14	1.4 (7)	C27—C28—C29—C30	29.6 (8)
N3—C12—C13—C14	−178.0 (4)	C75—C28—C29—C30	−84.5 (7)
N2—C12—C13—C21	−179.6 (4)	C69—C28—C29—C30	149.3 (7)
N3—C12—C13—C21	1.0 (4)	C25—C26—C30—C31	−0.9 (10)
C21—C13—C14—C15	−2.6 (6)	C27—C26—C30—C31	−180.0 (6)
C12—C13—C14—C15	176.3 (4)	C25—C26—C30—C29	179.3 (6)
C13—C14—C15—C19	2.9 (6)	C27—C26—C30—C29	0.2 (8)
C13—C14—C15—C16	−172.4 (4)	C28—C29—C30—C31	161.2 (7)
C14—C15—C16—C17	156.9 (4)	C28—C29—C30—C26	−18.9 (8)

C26—C30—C31—C32	1.6 (10)
C29—C30—C31—C32	−178.6 (7)
C25—C24—C32—C31	1.4 (8)
C23—C24—C32—C31	178.5 (5)
C25—C24—C32—C33	−177.7 (5)
C23—C24—C32—C33	−0.5 (5)
C30—C31—C32—C24	−1.8 (9)
C30—C31—C32—C33	177.0 (6)
C34—N6—C33—N5	2.6 (7)
C34—N6—C33—C32	−178.2 (4)
C23—N5—C33—N6	178.2 (5)
C23—N5—C33—C32	−1.0 (5)
C24—C32—C33—N6	−178.3 (4)
C31—C32—C33—N6	2.8 (9)
C24—C32—C33—N5	1.0 (6)
C31—C32—C33—N5	−177.9 (6)
C33—N6—C34—N7	2.5 (7)
C33—N6—C34—C35	179.9 (4)
C44—N7—C34—N6	176.7 (4)
C44—N7—C34—C35	−0.9 (5)
N6—C34—C35—C43	−177.4 (4)
N7—C34—C35—C43	0.4 (5)
N6—C34—C35—C36	0.3 (7)
N7—C34—C35—C36	178.1 (4)
C43—C35—C36—C37	1.0 (6)
C34—C35—C36—C37	−176.4 (4)
C35—C36—C37—C41	−0.6 (6)
C35—C36—C37—C38	177.8 (4)
C36—C37—C38—C39	−155.8 (5)
C41—C37—C38—C39	22.8 (5)
C37—C38—C39—C81	82.2 (4)
C37—C38—C39—C87	−154.6 (4)
C37—C38—C39—C40	−33.5 (4)
C38—C39—C40—C41	33.0 (4)
C81—C39—C40—C41	−82.9 (5)
C87—C39—C40—C41	151.9 (4)
C36—C37—C41—C42	−0.2 (7)
C38—C37—C41—C42	−178.9 (4)
C36—C37—C41—C40	177.4 (4)
C38—C37—C41—C40	−1.3 (5)
C39—C40—C41—C42	156.9 (5)
C39—C40—C41—C37	−20.4 (5)
C37—C41—C42—C43	0.6 (6)
C40—C41—C42—C43	−176.4 (4)
C36—C35—C43—C42	−0.6 (7)
C34—C35—C43—C42	177.3 (4)
C36—C35—C43—C44	−177.6 (4)
C34—C35—C43—C44	0.3 (5)
C41—C42—C43—C35	−0.2 (6)
C41—C42—C43—C44	175.9 (4)
C1—N8—C44—N7	0.7 (6)
C1—N8—C44—C43	−177.5 (4)
C34—N7—C44—N8	−177.4 (4)
C34—N7—C44—C43	1.1 (4)
C35—C43—C44—N8	177.7 (4)
C42—C43—C44—N8	1.1 (7)
C35—C43—C44—N7	−0.9 (5)
C42—C43—C44—N7	−177.4 (4)
C51—C6—C45—C46	178.5 (6)
C7—C6—C45—C46	57.1 (8)
C5—C6—C45—C46	−58.9 (8)
C6—C45—C46—C47	−175.3 (6)
C45—C46—C47—C48	179.9 (7)
C46—C47—C48—C49A	158.8 (14)
C46—C47—C48—C49B	−163.6 (10)
C47—C48—C49A—C50	152.8 (14)
C49B—C48—C49A—C50	66.5 (16)
C47—C48—C49B—C50	−172.3 (10)
C49A—C48—C49B—C50	−60.4 (13)
C48—C49A—C50—C49B	−68.9 (16)
C48—C49B—C50—C49A	59.0 (13)
C45—C6—C51—C52	53.5 (8)
C7—C6—C51—C52	178.1 (6)
C5—C6—C51—C52	−72.2 (7)
C6—C51—C52—C53B	−167.0 (11)
C6—C51—C52—C53A	157.3 (7)
C53B—C52—C53A—C54A	158 (3)
C51—C52—C53A—C54A	−90.4 (11)
C52—C53A—C54A—C55A	170.0 (10)
C53A—C54A—C55A—C56	56.0 (19)
C51—C52—C53B—C54B	−64 (2)
C53A—C52—C53B—C54B	20.7 (13)
C52—C53B—C54B—C55B	−73 (2)
C53B—C54B—C55B—C56	−107 (3)
C54A—C55A—C56—C55B	−15 (3)
C54B—C55B—C56—C55A	−130 (5)
C18—C17—C57—C58	−59.8 (5)
C63—C17—C57—C58	65.1 (5)
C16—C17—C57—C58	−173.4 (4)
C17—C57—C58—C59	180.0 (4)
C57—C58—C59—C60	−179.3 (5)
C58—C59—C60—C61	−174.3 (5)
C59—C60—C61—C62	−67.1 (9)
C18—C17—C63—C64	−60.4 (6)
C57—C17—C63—C64	175.5 (5)
C16—C17—C63—C64	53.1 (6)
C17—C63—C64—C65	87.9 (7)
C63—C64—C65—C66B	176.2 (12)
C63—C64—C65—C66A	−165.8 (6)
C66B—C65—C66A—C67A	−35.7 (17)
C64—C65—C66A—C67A	172.7 (9)
C65—C66A—C67A—C68A	56.2 (16)
C64—C65—C66B—C67B	174.3 (19)
C66A—C65—C66B—C67B	138 (3)
C65—C66B—C67B—C68B	165 (2)
C27—C28—C69—C70	−57.2 (11)
C75—C28—C69—C70	63.3 (11)
C29—C28—C69—C70	−172.1 (8)
C28—C69—C70—C71	−177.5 (9)
C69—C70—C71—C72	68.7 (14)
C70—C71—C72—C73B	71.2 (14)
C70—C71—C72—C73A	7 (3)
C71—C72—C73A—C74	110 (3)
C73B—C72—C73A—C74	32.6 (19)
C71—C72—C73B—C74	179.0 (12)
C73A—C72—C73B—C74	−33 (2)
C72—C73A—C74—C73B	−32.8 (19)
C72—C73B—C74—C73A	37 (2)
C27—C28—C75—C76	173.6 (7)
C29—C28—C75—C76	−74.6 (8)
C69—C28—C75—C76	50.7 (10)
C28—C75—C76—C77	172.8 (8)
C75—C76—C77—C78	58.4 (13)
C76—C77—C78—C79	169.5 (10)

C77—C78—C79—C80	179.1 (11)
C38—C39—C81—C82	66.2 (6)
C87—C39—C81—C82	−56.6 (6)
C40—C39—C81—C82	176.8 (4)
C39—C81—C82—C83	−174.6 (5)
C81—C82—C83—C84	171.4 (6)
C82—C83—C84—C85	−175.5 (8)
C83—C84—C85—C86	172.1 (12)
C38—C39—C87—C88	−179.7 (5)
C81—C39—C87—C88	−57.5 (6)
C40—C39—C87—C88	66.8 (6)
C39—C87—C88—C89	174.8 (5)
C87—C88—C89—C90	173.2 (5)
C88—C89—C90—C91	−179.5 (5)
C89—C90—C91—C92	173.4 (6)
C103—N9—C93—N12^{i}	−178.3 (4)
C103—N9—C93—C94	0.3 (5)
N12^{i}—C93—C94—C102	177.7 (4)
N9—C93—C94—C102	−0.9 (5)
N12^{i}—C93—C94—C95	−1.1 (7)
N9—C93—C94—C95	−179.8 (4)
C102—C94—C95—C96	−1.2 (6)
C93—C94—C95—C96	177.5 (4)
C94—C95—C96—C100	−0.4 (6)
C94—C95—C96—C97	−175.9 (4)
C95—C96—C97—C98	−170.1 (4)
C100—C96—C97—C98	14.0 (5)
C96—C97—C98—C121	−141.3 (4)
C96—C97—C98—C115	91.8 (4)
C96—C97—C98—C99	−22.7 (5)
C121—C98—C99—C100	142.0 (5)
C115—C98—C99—C100	−92.7 (5)
C97—C98—C99—C100	23.6 (5)
C95—C96—C100—C101	2.2 (6)
C97—C96—C100—C101	178.4 (4)
C95—C96—C100—C99	−174.9 (4)
C97—C96—C100—C99	1.3 (5)
C98—C99—C100—C101	167.2 (4)
C98—C99—C100—C96	−16.0 (5)
C96—C100—C101—C102	−2.1 (6)
C99—C100—C101—C102	174.3 (4)
C100—C101—C102—C94	0.5 (6)
C100—C101—C102—C103	−178.2 (4)
C95—C94—C102—C101	1.2 (6)
C93—C94—C102—C101	−177.8 (4)
C95—C94—C102—C103	−179.8 (4)
C93—C94—C102—C103	1.2 (4)
C104—N10—C103—N9	0.9 (7)
C104—N10—C103—C102	−179.7 (4)
C93—N9—C103—N10	179.9 (4)
C93—N9—C103—C102	0.4 (4)
C101—C102—C103—N10	−1.7 (7)
C94—C102—C103—N10	179.5 (4)
C101—C102—C103—N9	177.8 (4)
C94—C102—C103—N9	−1.0 (4)
C103—N10—C104—N11	−1.8 (7)
C103—N10—C104—C105	177.9 (4)
C114—N11—C104—N10	179.3 (4)
C114—N11—C104—C105	−0.4 (5)
N10—C104—C105—C106	1.2 (8)
N11—C104—C105—C106	−179.1 (5)
N10—C104—C105—C113	−179.0 (4)
N11—C104—C105—C113	0.7 (5)
C113—C105—C106—C107	0.9 (8)
C104—C105—C106—C107	−179.4 (5)
C105—C106—C107—C111	0.3 (8)
C105—C106—C107—C108	−178.8 (6)
C106—C107—C108—C109	−162.0 (6)
C111—C107—C108—C109	18.9 (7)
C107—C108—C109—C133	86.6 (6)
C107—C108—C109—C127	−149.8 (5)
C107—C108—C109—C110	−29.9 (7)
C133—C109—C110—C111	−86.4 (6)
C108—C109—C110—C111	30.2 (7)
C127—C109—C110—C111	150.0 (6)
C106—C107—C111—C112	−0.6 (9)
C108—C107—C111—C112	178.6 (5)
C106—C107—C111—C110	−178.7 (6)
C108—C107—C111—C110	0.6 (7)
C109—C110—C111—C112	162.6 (6)
C109—C110—C111—C107	−19.5 (7)
C107—C111—C112—C113	−0.2 (8)
C110—C111—C112—C113	177.4 (6)
C106—C105—C113—C112	−1.7 (8)
C104—C105—C113—C112	178.5 (4)
C106—C105—C113—C114	179.1 (4)
C104—C105—C113—C114	−0.7 (5)
C111—C112—C113—C105	1.3 (8)
C111—C112—C113—C114	−179.8 (5)
C93^{i}—N12—C114—N11	1.9 (7)
C93^{i}—N12—C114—C113	−179.5 (4)
C104—N11—C114—N12	178.7 (4)
C104—N11—C114—C113	−0.1 (5)
C105—C113—C114—N12	−178.3 (4)
C112—C113—C114—N12	2.7 (8)
C105—C113—C114—N11	0.5 (5)
C112—C113—C114—N11	−178.5 (5)
C121—C98—C115—C116	−53.7 (7)
C97—C98—C115—C116	71.1 (6)
C99—C98—C115—C116	−177.0 (5)
C98—C115—C116—C117	−167.2 (6)
C115—C116—C117—C18A	64.0 (13)
C115—C116—C117—C18B	86.5 (12)
C116—C117—C18A—C19A	72.6 (16)
C18B—C117—C18A—C19A	25.3 (19)
C117—C18A—C19A—C20A	−175.9 (16)
C18A—C117—C18B—C19B	−42.8 (19)
C116—C117—C18B—C19B	175.2 (19)
C117—C18B—C19B—C20B	178 (2)
C115—C98—C121—C122	−60.4 (7)
C97—C98—C121—C122	175.1 (5)
C99—C98—C121—C122	61.1 (7)
C98—C121—C122—C123	−161.5 (6)
C121—C122—C123—C124	−173.6 (6)
C122—C123—C124—C125	−173.4 (6)
C123—C124—C125—C126	177.1 (7)
C133—C109—C127—C128	−61.2 (8)
C108—C109—C127—C128	176.2 (6)
C110—C109—C127—C128	61.3 (9)
C109—C127—C128—C129	−179.8 (7)
C127—C128—C129—C130	174.9 (8)
C128—C129—C130—C131	58.4 (11)
C129—C130—C131—C132	174.8 (7)
C108—C109—C133—C134	70.6 (7)

C127—C109—C133—C134	−53.1 (8)	C134—C135—C36A—C37A	−175.2 (19)
C110—C109—C133—C134	−176.9 (6)	C135—C36A—C37A—C38A	−97 (6)
C109—C133—C134—C135	−156.2 (13)	C134—C135—C36B—C37B	−164 (2)
C133—C134—C135—C36B	−23 (3)	C36A—C135—C36B—C37B	−79 (3)
C133—C134—C135—C36A	−69.9 (19)	C135—C36B—C37B—C38B	125 (3)
C36B—C135—C36A—C37A	67 (3)		

Symmetry codes: (i) $2-x, 1-y, 1-z$.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C47
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C6
C7
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C5
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C53B
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C53A
C3
C9
C54B
C2
C54A
C55B
C1
C10
C55A
C56
N8
C11
N2
C14
C16
C92
C85
C90
C83
C88
C81
C40
C42
C43
C44
N1
C12
C13
C15
C57
C80
C86
C91
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C89
C82
C87
C39
C41
N7
N3
C17
C59
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C34
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C63
C18
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C38
C35
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C66A
C60
C36
N6
N4
C23
C65
C80
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C32
C24
C67A
C66B
C78
C31
C25
C67B
C77
C30
C26
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C70
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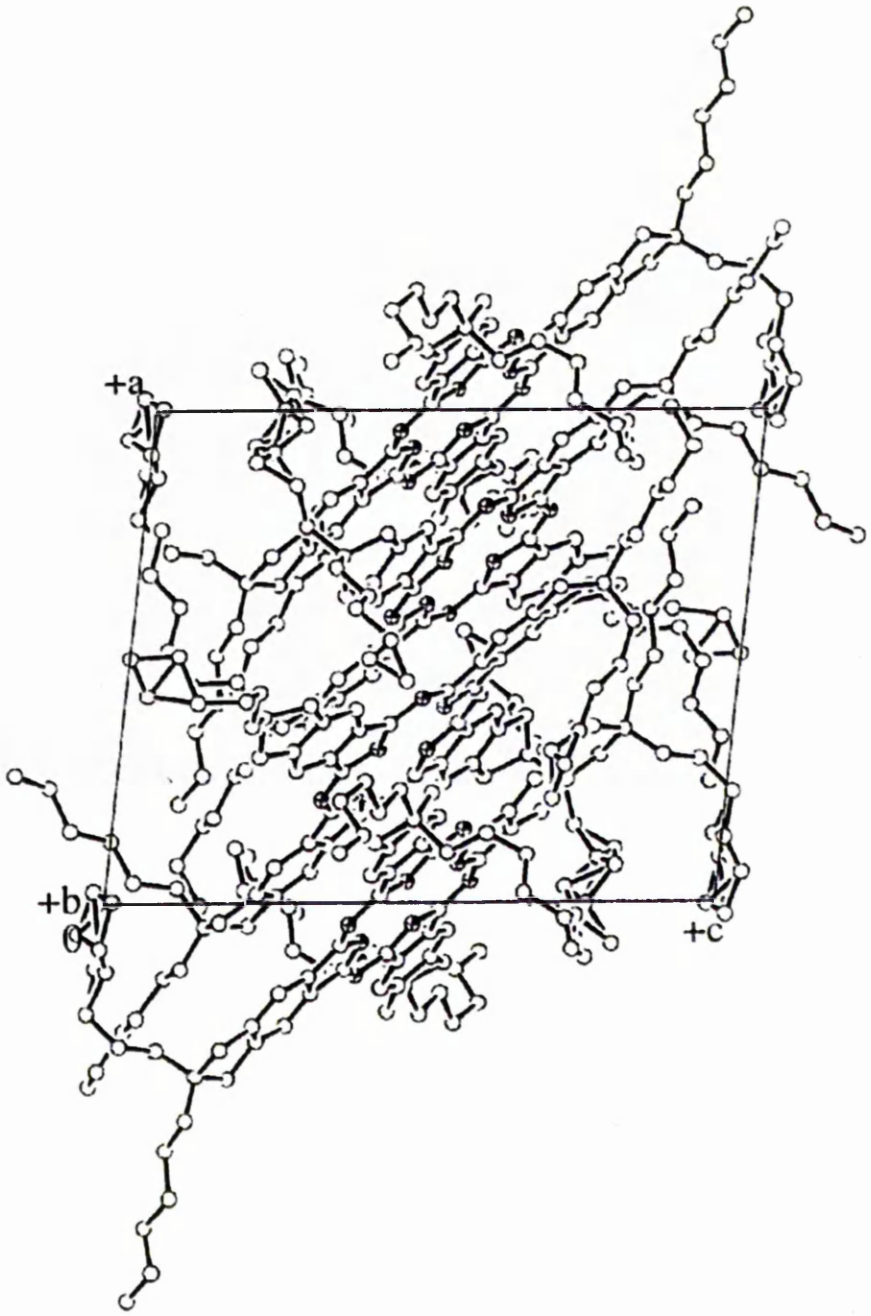
C71
C73A
C72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+b
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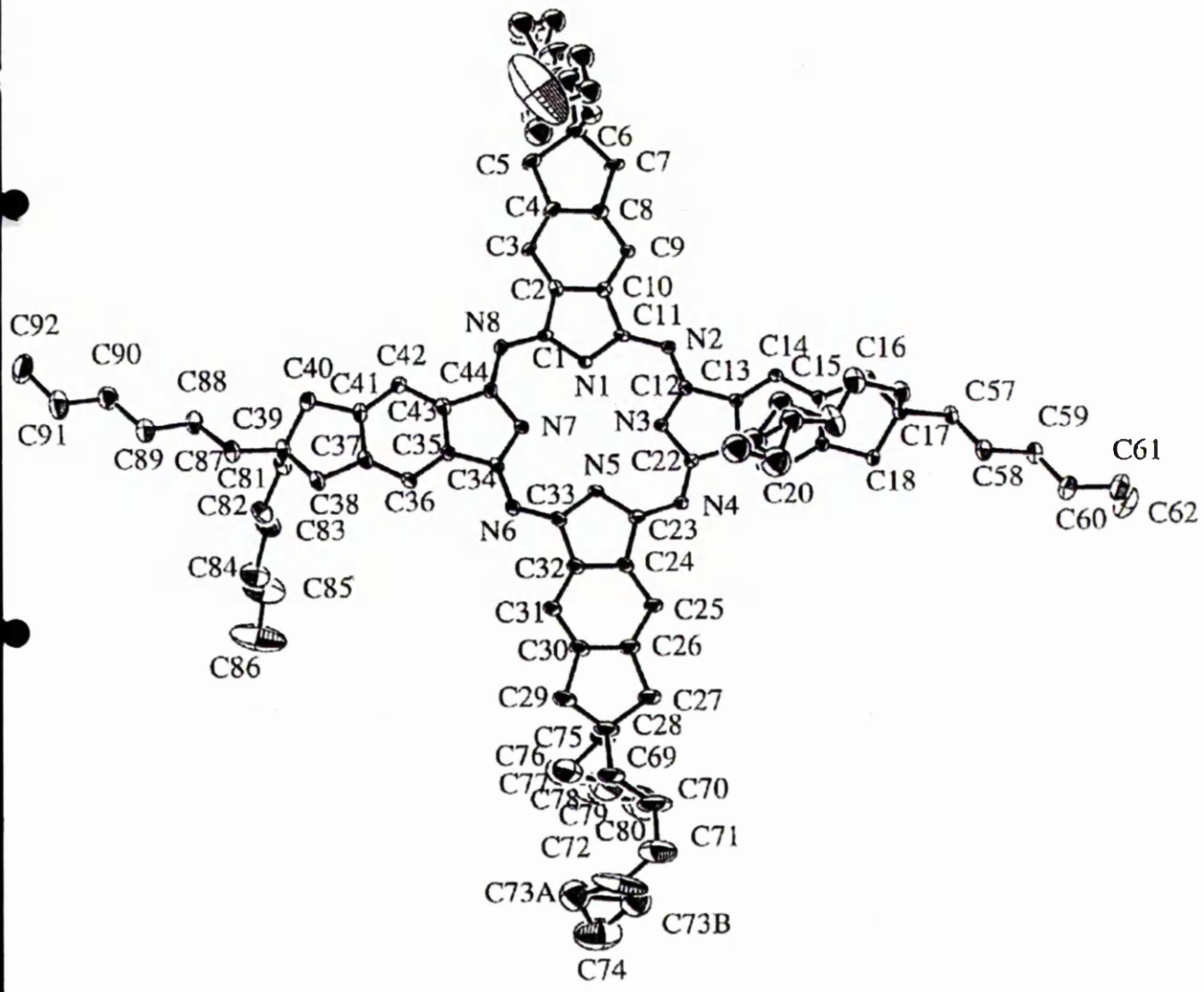
+c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N8
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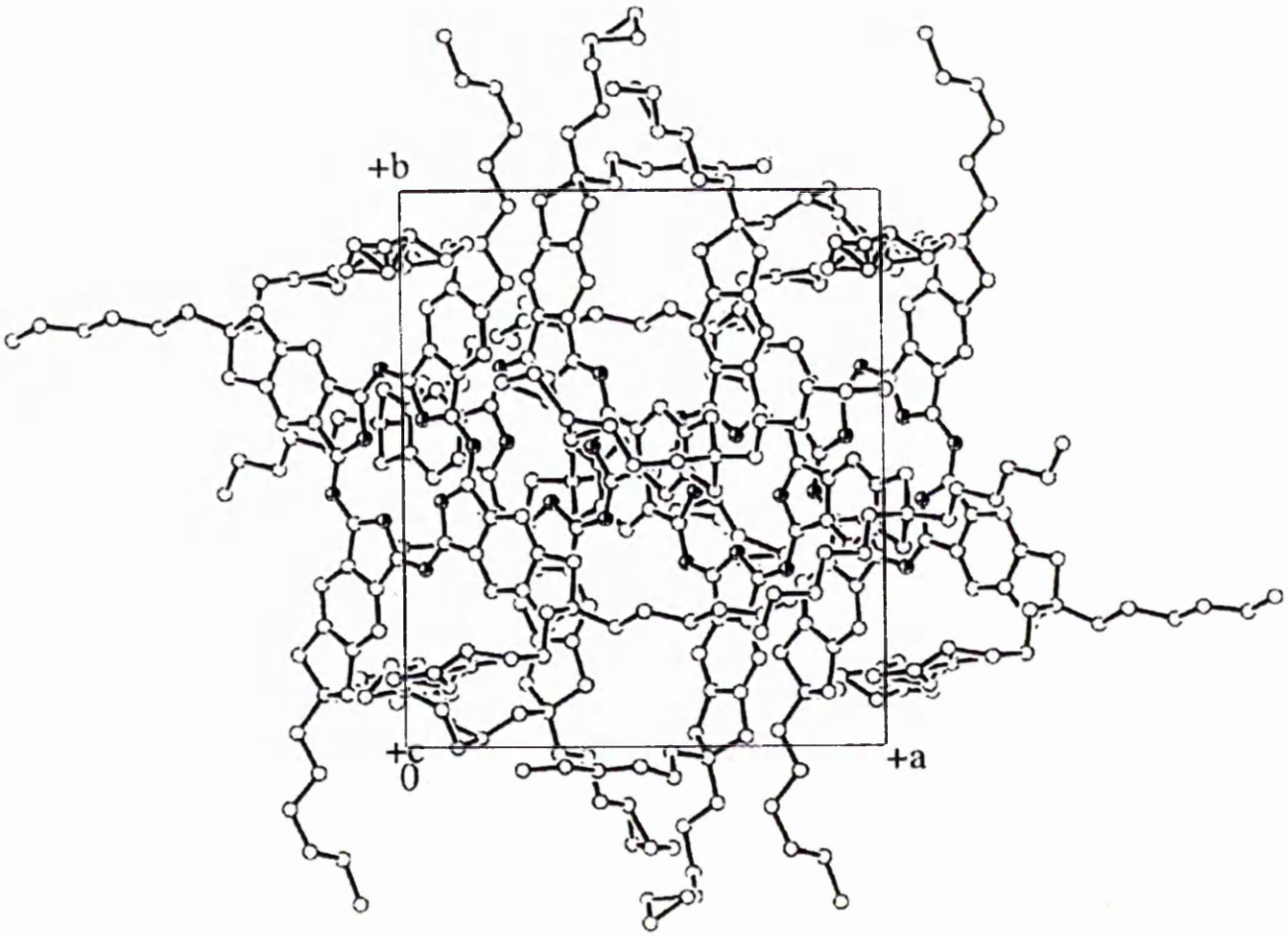
C73B
C74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+c
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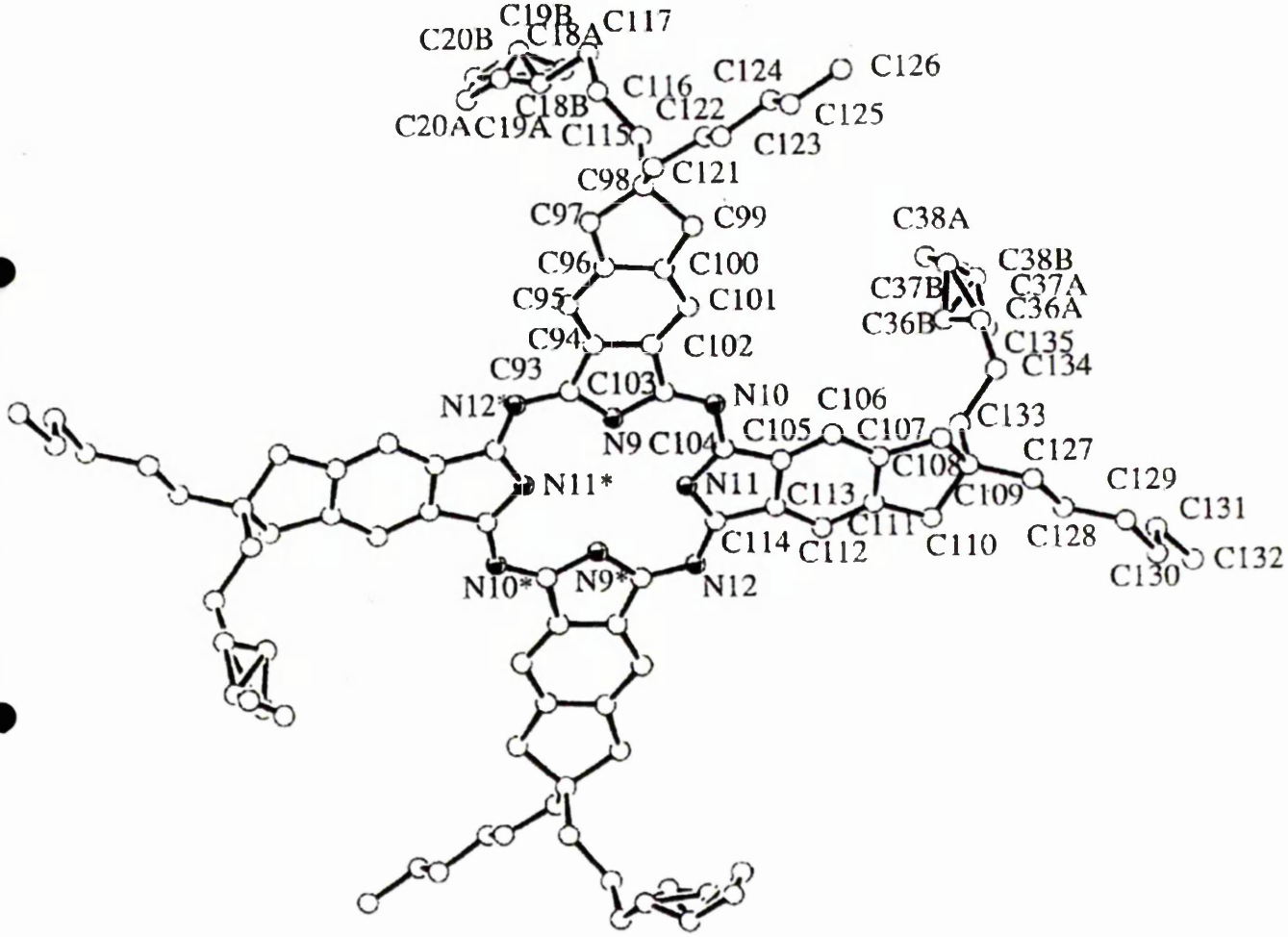
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C18A
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C126
C116
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C125
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C19A
C115
C123
C98
C121
C97
C99
C38A
C96
C100
C38B
C37B
C37A
C95
C101
C36A
C36B
C135
C94
C102
C134
C93
C103
N10
C106
N12*
C133
N9
C104
C105
C107
C127
N11*
N11
C108
C129
C113
C109
C131
C114
C112
C111
C110
C128
C132
N10*
N9*
N12
C130