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SYNTHESIS OF MULTI-NEOPENTOXY SUBSTITUTED AND NON-CENTROSYMMETRIC PHTHALOCYANINES

NAMRTA BHARDWAJ

A thesis submitted to the Faculty of Graduate Studies
in partial fulfillment of the requirements
of the degree of

DOCTOR OF PHILOSOPHY

Graduate Programme in Chemistry
York University
Toronto, Ontario, Canada

April 2001

SYNTHESIS OF MULTI-NEOPENTOXY SUBSTITUTED AND NON-CENTROSYMMETRIC PHTHALOCYANINES

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ABSTRACT

A series of phthalonitriles substituted with neopentoxy groups in the 4,5-, 3,6- and 3,4,5,6- positions were synthesized, characterized and subsequently condensed to their corresponding phthalocyanines. The UV-Vis spectrum of the 1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-hexadecaneopentoxyphthalocyanine was found to be more red shifted than any other hexadecaalkoxy substituted phthalocyanine reported in the literature thus far.

The development of a synthetic method toward the preparation of tetrasubstituted phthalonitriles consisting of amino-alkoxy and amino-thiol substituents is also described. This method involves the reaction of 3,4,5,6-tetrafluorophthalonitrile with an amine to yield 4,5-diamino-3,6-difluorophthalonitrile. Further reaction of this compound with either an alcohol or thiol afforded tetrasubstituted phthalonitriles. Self-condensation of these phthalonitriles was not possible, however, cross condensation reaction of these compounds with phthalonitrile afforded non-centrosymmetric phthalocyanines. In addition, a method for synthesizing a non-centrosymmetric phthalocyanine using monomeric and dimeric phthalocyanine intermediates was examined.

Furthermore, it was discovered that the ^{1}H NMR spectra of the neopentoxy substituted phthalocyanines displayed signs of restricted rotation. Thus, five of the neopentoxy substituted phthalocyanines were subjected to variable temperature ^{1}H NMR studies and their thermokinetic parameters were determined.

ACKNOWLEDGEMENTS

I sincerely wish to thank Dr. Clifford C. Leznoff for his continual support and guidance throughout the course of this work. I would also like to thank the staff and faculty members of the Chemistry Department at York University, especially Dr. Potvin and Dr. Aspinall, for their support during this work. I am also grateful for the friendship, support and invaluable suggestions which I received over the years from Dr. Jailall Ramnauth, Anna D'Ascanio, Bob Suchozak, Dr. Ashot Khanamiryan, Christos Alexiou, Dr. Zhaopeng Li, Dr. S. Zeki Yildiz, Michelle Delaney-Luu, Scott Black, Sandra Agostino, Amir Lackpour and Dr. John Andraos.

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LIST OF ABBREVIATIONS

^{13}C-NMR	carbon nuclear magnetic resonance
^{1}H-NMR	proton nuclear magnetic resonance
Anal. Calcd.	elemental analysis calculated (%)
br	broad
C	Celsius
cm^{-1}	wavenumbers
d	doublet
dd	doublet of doublets
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DMAE	2-N,N-dimethylaminoethanol
DMF	N,N-dimethylformamide
EI	electron impact
FAB	fast atom bombardment
FT	Fourier transform
g	grams
h	hours
HMPA	hexamethylphosphoramide
HRMS	high resolution mass spectrometry
Hz	Hertz

IR	infrared
J	coupling constant
K	Kelvin
lit.	literature
m	multiplet
m/z	mass to charge ratio
M	metal
M+	molecular ion
MALDI	matrix assisted laser desorption ionization
mg	milligrams
mL	milliliters
mmol	millimoles
mp	melting point
MS	mass spectrum
NLO	non-linear optics
nm	nanometers
Pc(s)	phthalocyanine(s)
ppm	parts per million
q	quartet
R	substituent

r.t.	room temperature
s	singlet
s	strong
subPc	subphthalocyanine
t	triplet
THF	tetrahydrofuran
TLC	thin layer chromatography
UV	ultraviolet
Vis	visible
vs	very strong
w	weak

INTRODUCTION

Background

Phthalocyanines (Pcs) (**1**), first discovered in the early 1900's, are among the first macrocyclic molecules ever synthesized [1]. Braun and Tcherniac carried out the first recorded synthesis of a phthalocyanine (Pc) in 1907 by self-condensing *o*-cyanobenzamide at high temperature [2]. Similarly, in 1927, de Diesbach and von der Weid obtained an exceptionally stable blue material, copper(II) Pc, during the reaction of *o*-dibromobenzene with copper cyanide in refluxing pyridine [3]. A year later, during an industrial preparation of phthalimide from phthalic anhydride, a glass-lined reaction vessel cracked, exposing the outer steel casing to the reaction, which resulted in the formation of a blue-green material. This iron-containing by-product was an exceptionally stable and insoluble pigment [4].

The structure of unsubstituted phthalocyanine (**1**), Fig. 1, which is a symmetrical macrocycle composed of four iminoisoindoline units with a central cavity of sufficient size to accommodate various metal ions, was determined in the 1930's by Lindstead's group [5-10]. This structure was later confirmed by the X-ray diffraction analysis of Robertson [11].

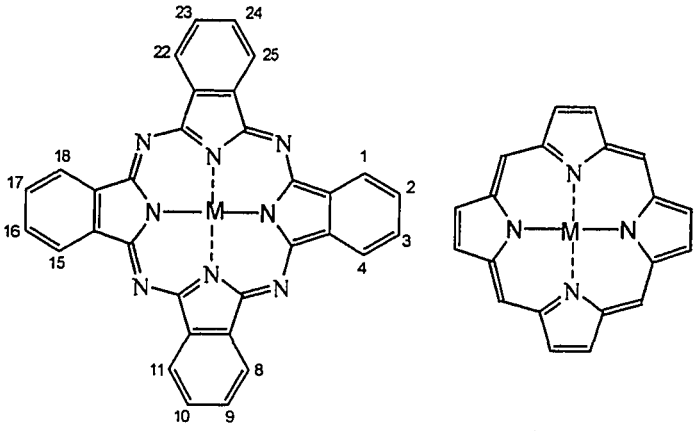


Figure 1: Structure of unsubstituted phthalocyanine (**1**) and porphine (**2**)

Structurally, phthalocyanines are very similar to porphyrins, **2**, and are therefore often referred to as tetraazatetrabenzoporphyrins [12]. Phthalocyanines are composed of four isoindole moieties joined together by aza nitrogens whereas porphyrins are composed of four pyrrole moieties joined together by methine (-CH=) groups. Addition of the four peripheral benzo units in phthalocyanines causes greater delocalization of the 18-π electron conjugation of the inner core in comparison with porphyrins, which results in the electronic spectrum of phthalocyanines shifting to lower energy relative to porphyrins. Substitution of the reactive methine groups by aza nitrogens results in

phthalocyanines having greater chemical stability in comparison with porphyrins [2, 13].

Due to their unique properties which include extremely high thermal stability, inertness to acids and alkalis, insolubility in most solvents, high dyeing power and color intensity, phthalocyanines have attracted a great deal of interest [14]. Traditionally, these properties ensured the wide application of Pcs as dyes and pigments in the painting, printing and textile industries [14]. Recently, however, phthalocyanine chemistry has been undergoing a renaissance since these compounds display a potential for application in a wide variety of fields, including photodynamic therapy of cancer, chemical sensors, molecular metals, electrochromic display devices, and redox electrocatalysts [1].

General Synthesis of Phthalocyanines

Due to the potential application of phthalocyanines in numerous fields, many methods have been developed for their synthesis. Initial synthetic strategies involved the use of compounds such as *o*-cyanobenzamide or phthalic anhydride as precursors. Now, however, phthalonitrile is the most commonly used precursor in phthalocyanine synthesis.

A commonly employed synthetic route to preparing phthalocyanines involves treating phthalonitrile (**3**) with sodium or lithium pentoxide in refluxing 1-

pentanol to yield the corresponding disodium or dilithium Pc (**1b**). Demetallation to the corresponding metal-free phthalocyanine (**1a**) can be achieved by the addition of concentrated sulfuric acid, Scheme 1.

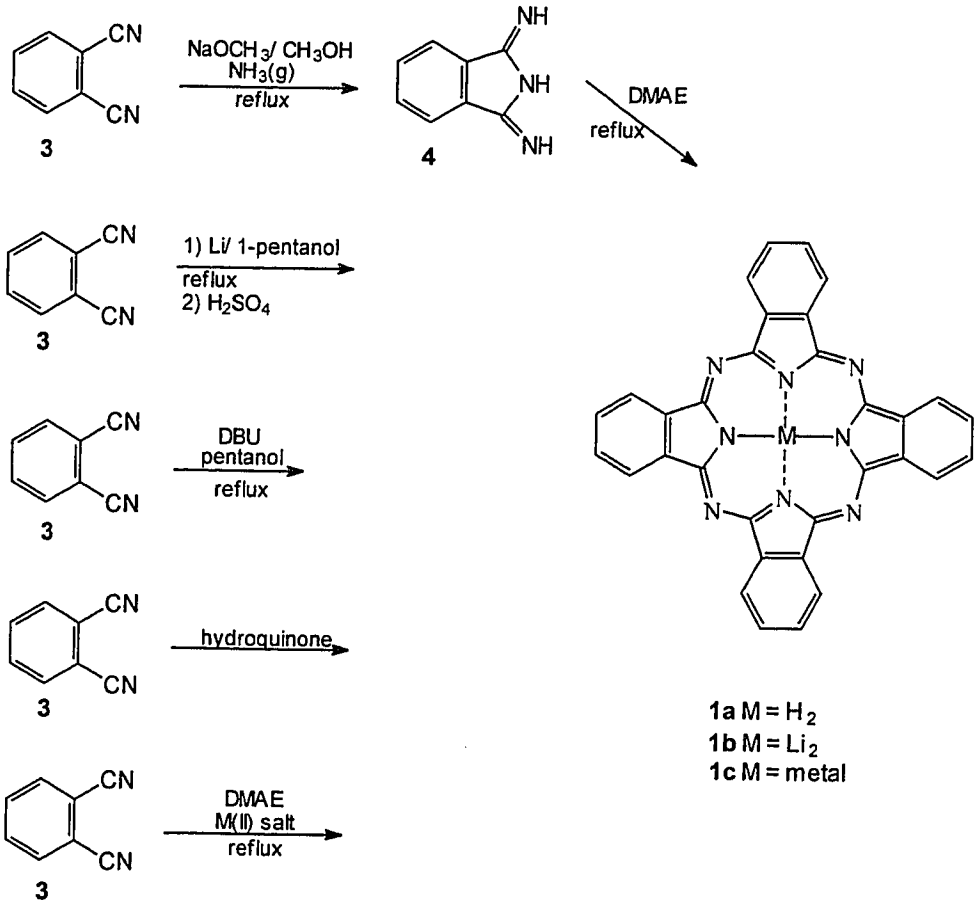
Alternatively, phthalonitrile (**3**) can also undergo cyclotetramerization in a melt with hydroquinone, which is required as a reducing agent. This method allows metal-free phthalocyanine (**1a**) to be prepared in the absence of any metal ions that may be incorporated into the product as a metallated phthalocyanine impurity, Scheme 1 [15].

Furthermore, the addition of ammonia gas into a sodium methoxide/ methanol solution converts **3** to diiminoisolindoline (**4**) [16], which can subsequently be condensed, in refluxing N,N-dimethylaminoethanol (DMAE), to metal-free Pc (**1a**) (Scheme 1).

Generally, numerous metals can replace the two internal hydrogens of metal-free Pcs to yield metallophthalocyanines (**1c**) (Scheme 1) [17]. Most commonly, metallated phthalocyanines are prepared directly from **3** or **4** using the metal ion as a template for the cyclotetramerization. Milder conditions involve condensing **3** in the presence of a metal salt in 1-pentanol with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) or 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) as a non-nucleophilic organic base [17, 18].

Alternatively, H_2Pc (**1a**) or Li_2Pc (**1b**) can react with numerous metal salts to yield the corresponding metallated phthalocyanine (**1c**). Unfortunately,

due to the highly insoluble nature of most H_2Pcs in many organic solvents, high boiling aromatic solvents are required to ensure complete metallation [3].



Scheme 1. Various methods for the synthesis of phthalocyanine

Approximately seventy different elemental ions can be placed in the central cavity of phthalocyanines and their physical properties are greatly influenced by the choice of the central metal [3,19]. Phthalocyanines usually

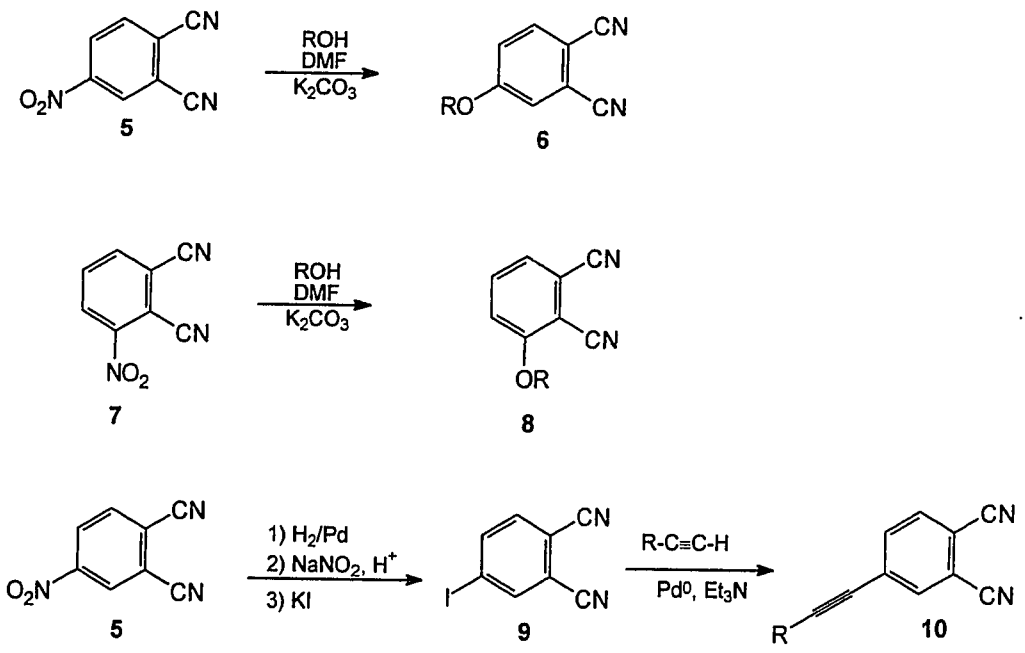
exist as a dianion (Pc^{2-}) which tightly holds many ions with an oxidation state of +2 such as Cu^{2+}, Co^{2+} and Fe^{2+}. It is difficult to remove most metals from the central cavity of Pcs without destroying the macrocycle. Metal cations with an oxidation state of +1 can also be incorporated into the central cavity. However, in this case, the central nitrogen atoms ligate two ions. Since both of these cations cannot be accommodated in the central cavity, the metal ions protrude from the plane of the phthalocyanine ring [3].

Phthalocyanines possess an extended π–conjugated electron system which permits π stacking (aggregation) between planar macrocycles, provided the distance between the macrocycles is small [20]. It is this intermolecular interaction between the macrocyles that causes phthalocyanines to be virtually insoluble in common organic solvents and thus limits their applications [20]. As mentioned above, when phthalocyanines contain alkali metals in the central cavity, the ions protrude from the plane of the Pc ring, resulting in a disruption of the π-stacking between the macrocycles [3]. Therefore, enhanced solubility in polar organic solvents is observed with alkali metal derivatives such as Li_2Pc or Na_2Pc. In addition to this, adding substituents to the periphery of the phthalocyanine increases their solubility since these substituents contribute to an increase in the distance between the stacked macrocycles and enable their solvation [20]. Although a maximum of sixteen substituents can be added to the periphery of the Pc macrocycle, the most commonly synthesized Pcs contain

only four or eight substituents. Symmetrically octasubsituted Pcs are usually less soluble than their tetrasubstituted analogues, since the latter are synthesized as a mixture of four isomers, which results in a lower degree of order in the solid state and hence increased solubility [21].

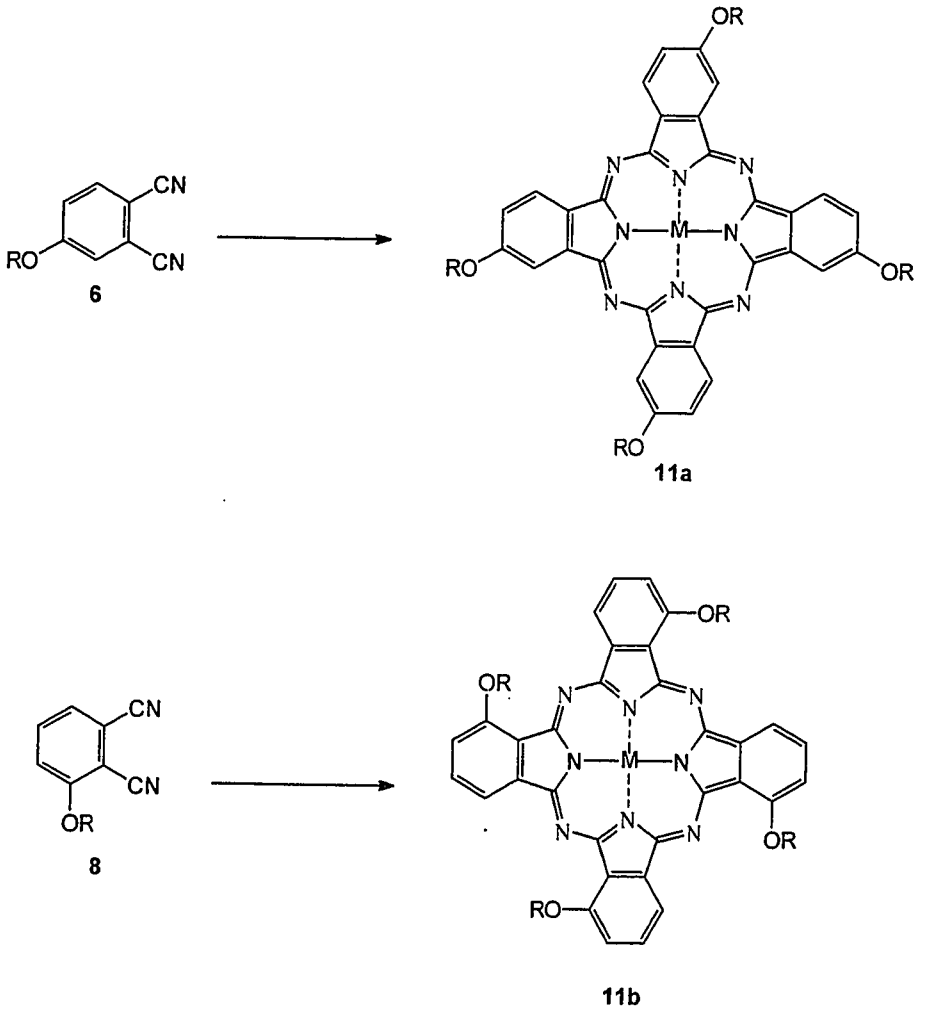
Synthesis of Tetra- and Octasubstituted Phthalocyanines

A variety of synthetic pathways exist for synthesizing either 3- or 4-substituted phthalonitriles, as shown in Scheme 2. A commonly employed and versatile route toward the preparation of phthalonitriles substituted with an ether linkage involves the treatment of 4-nitrophthalonitrile (**5**) or 3-nitrophthalonitrile (**7**) with an alcohol via an aromatic nucleophilic substitution reaction in N,N-dimethylformamide (DMF) in the presence of K_2CO_3 to give 4-alkoxyphthalonitriles (**6**) and 3-alkoxyphthalonitriles (**8**), Scheme 2 [22, 23]. In addition to this, **5** can be converted to 4-iodophthalonitrile (**9**) by the reduction of NO_2 followed by diazotization and treatment with KI. Subsequent reaction with alkynes in metal-catalyzed cross coupling-reactions yields alkynylphthalonitriles (**10**), Scheme 2 [24].



Scheme 2. Synthesis of 3- or 4-substituted phthalonitriles

Condensation of monosubstituted phthalonitriles yields tetrasubstituted phthalocyanines (**11a** and **11b**) (Scheme 3) as mixtures of four constitutional isomers with D_{2h}, C_{4h}, C_{2v}, and C_s symmetry in a 1:1:2:4 ratio. These isomers, for the substituted phthalocyanines derived from 4-substituted phthalonitriles, are shown in Figure 2; similar isomers are present for the substituted phthalocyanines derived from 3-substituted phthalonitriles.



Scheme 3: Synthesis of tetrasubstituted phthalocyanines

Unfortunately, this mixture of isomers is unavoidable when 4-substituted phthalonitriles are condensed to their corresponding phthalocyanine and, due to the strong tendency of phthalocyanines to aggregate in solution, separation of these isomers requires exhaustive chromatography, usually by preparative high performance liquid chromatography (HPLC) [25]. Separation can be avoided if

only one isomer is formed preferentially over the others. In the case of 4-substituted phthalonitriles, neither steric nor electronic effects of the substituents

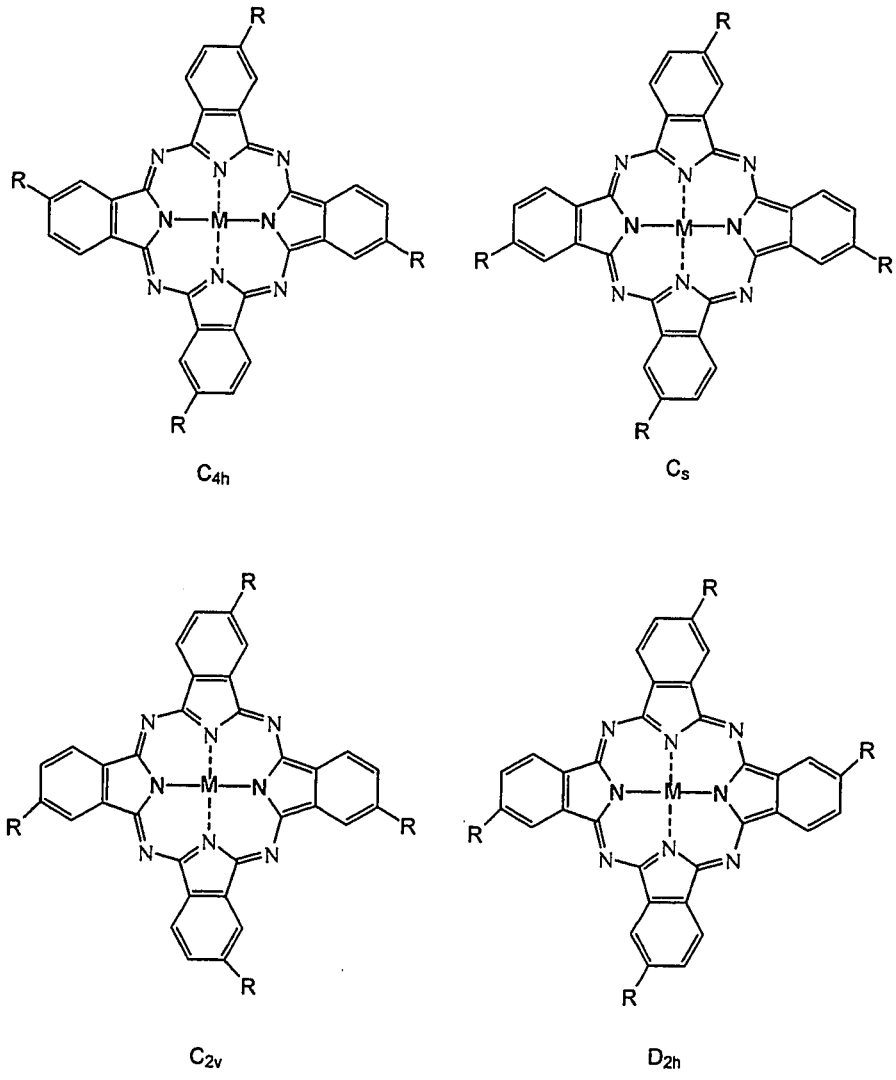
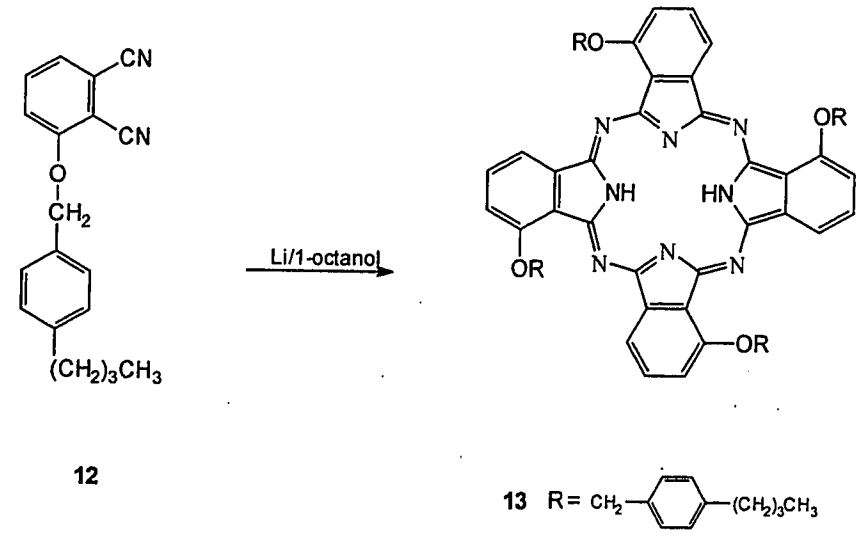


Figure 2. Constitutional isomers of tetrasubstituted phthalocyanines

are able to act as the driving force for a regioselective ring closure [26]. However, in the case of 3-substituted phthalonitriles, electronic and steric effects

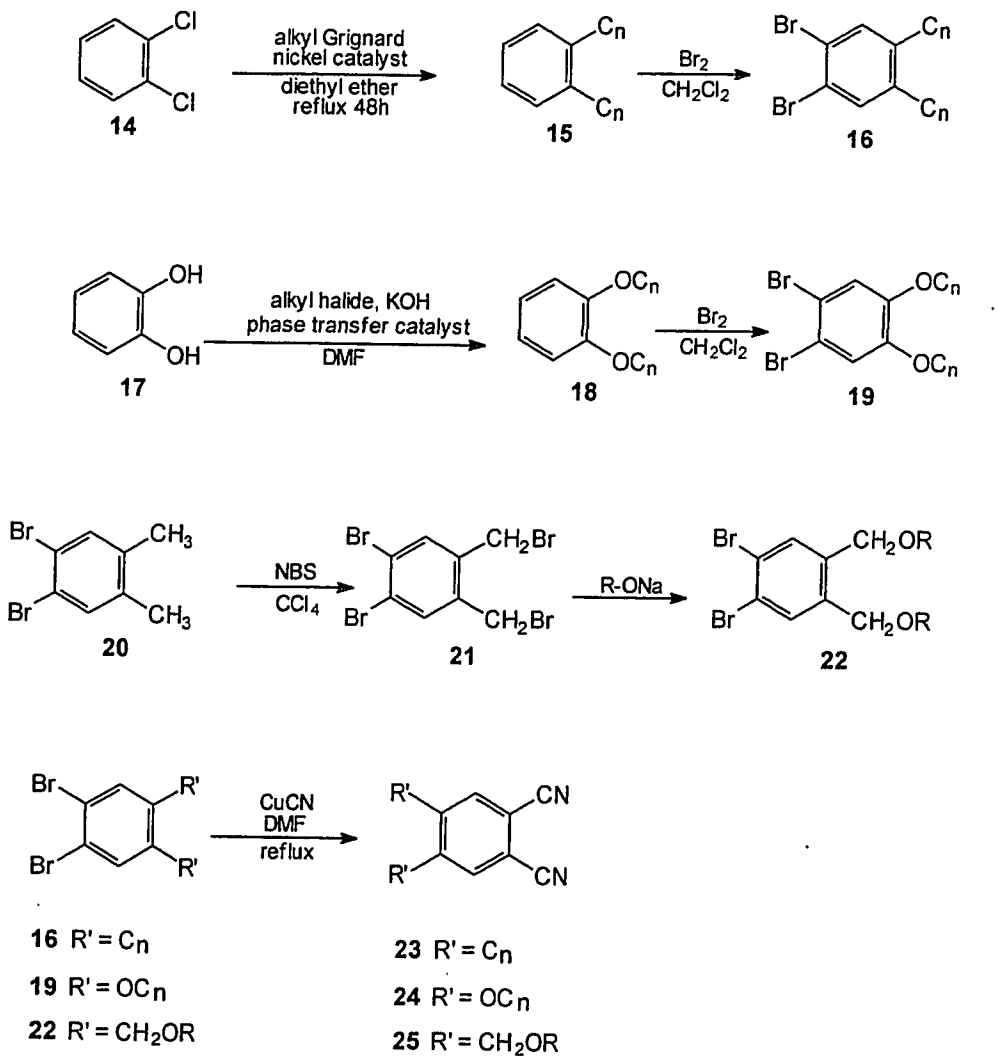
can strongly influence the ratio in which isomers are formed and thus give rise to a non-statistical distribution of compounds in instances where sterically demanding substituents are present [26-28]. When 3-(*p*-*n*-butylbenzyloxy) phthalonitrile (**12**) is self-condensed at low temperature, exclusive formation of the C_{4h} isomer (**13**) is observed, Scheme 4 [29]. In comparison with all of the possible isomers that may form, the C_{4h} isomer possesses the weakest steric interactions.



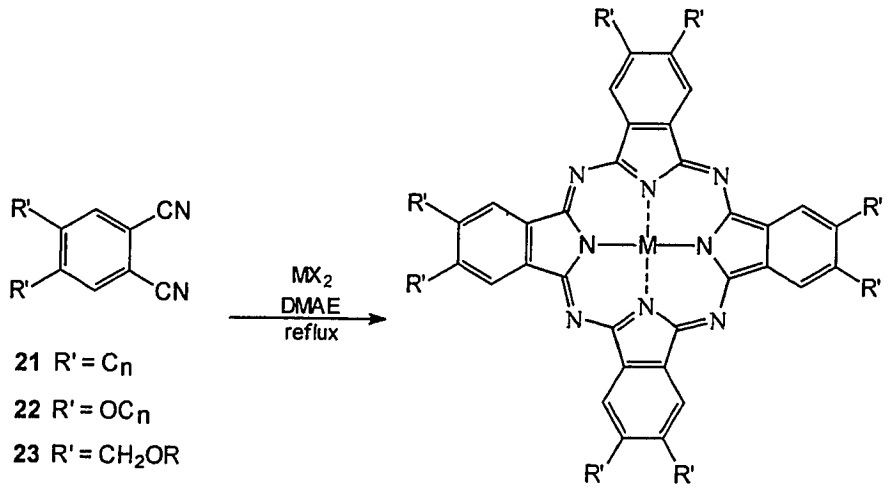
Scheme 4. Synthesis of a single constitutional isomer

Unlike the synthesis of tetrasubstituted phthalocyanines, octasubstituted Pcs can be obtained as single isomers if symmetrically substituted phthalonitriles are condensed. A variety of methods can be chosen for the synthesis of 4,5-

disubstituted phthalonitriles, depending on the linking group between the aromatic ring and the flexible alkyl chain, Scheme 5. For 4,5-disubstituted phthalonitriles, the alkyl side chain may be attached by a simple covalent bond, an ether or an oxymethylene moiety [30-33]. Addition of an alkyl side chain may be achieved by treatment of 1,2-dichlorobenzene (**14**) with an alkyl Grignard to yield the 1,2-dialkylbenzene, **15**, Scheme 5. Bromination of **15** yields the phthalonitrile precursor, 1,2-dialkyl-4,5-dibromobenzene (**16**). Alternatively, *o*-alkylation of catechol (**17**) yields 1,2-dialkyoxybenzene (**18**), which can be converted to 1,2-dialkoxy-4,5-dibromobenzene (**19**) by treatment with bromine. Furthermore, the addition of oxymethylene moieties can be achieved by α-bromination of 4,5-dibromoxylene (**20**) to yield (**21**). Subsequent treatment of **21** with an alkoxide forms the oxymethylene linkage of compound **22**. In all of the above mentioned syntheses, a common intermediate, a 1,2-dibromobenzene derivative (**16**, **19**, **22**), is formed. Conversion of this intermediate involves the displacement of bromine using copper(I) cyanide in refluxing DMF to give the corresponding phthalonitrile (**23-25**), Scheme 5. A common side product obtained in this reaction is the corresponding copper phthalocyanine. Thus, if formation of phthalocyanine, other than CuPc is required, then careful purification of the phthalonitrile is necessary [3]. In general, metallophthalocyanines (**26a-c**) are obtained by the condensation of the phthalonitriles **23-25** in the presence of the appropriate metal salt, Scheme 6.



Scheme 5. Synthesis of 4,5-disubstituted phthalonitriles



21 R' = C_n

22 R' = OC_n

23 R' = CH_2OR

26a R' = C_n

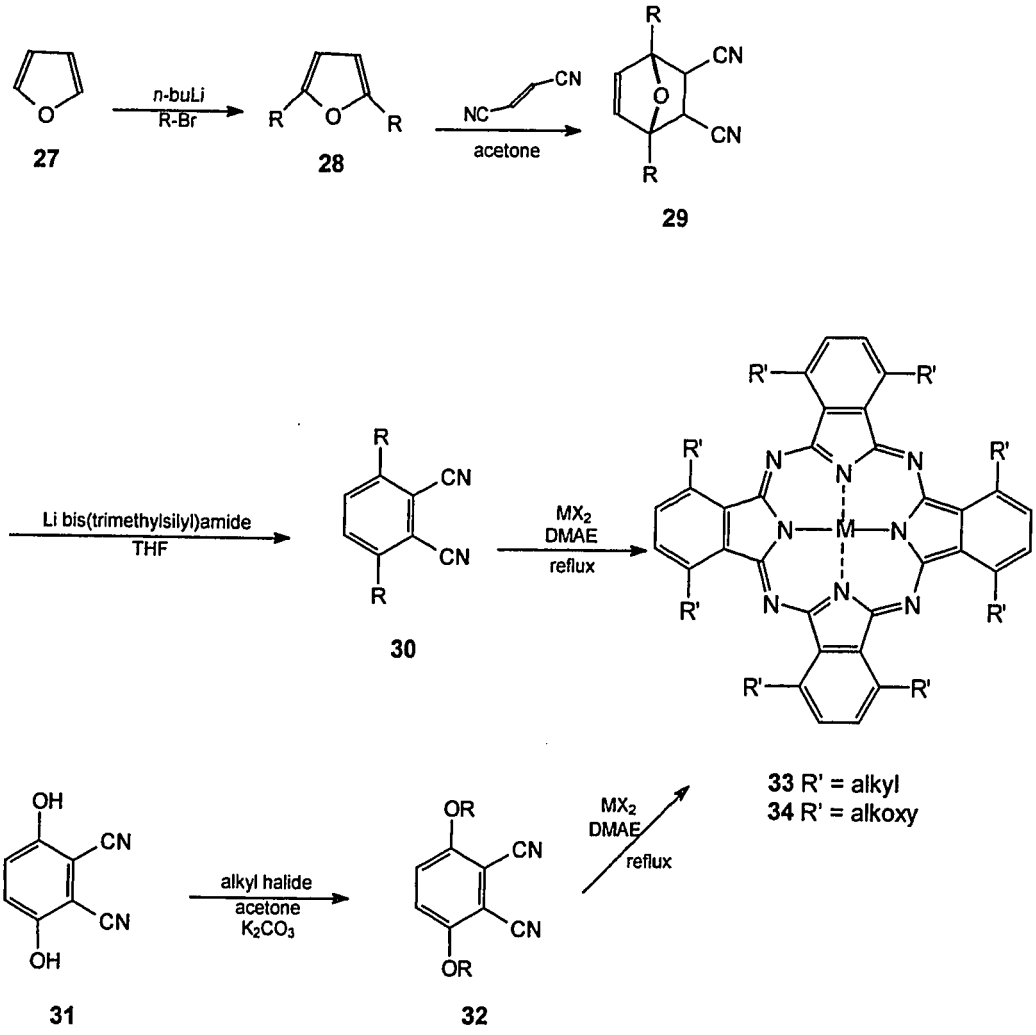
26b R' = OC_n

26c R' = CH_2OR

Scheme 6. Synthesis of 2,3,9,10,16,17,23,24-octasubstituted phthalocyanines

Alternative precursors for the synthesis of octasubstituted phthalocyanines are 3,6-dialkylphthalonitriles, which are formed from appropriately substituted 2,5-dialkylfurans as shown in Scheme 7. Alkylation of furan (**27**) yields **28** which is subsequently reacted with fumaronitrile in a Diels-Alder reaction to give the cycloaddition product **29**. Treatment of **29** with Li bis-(trimethylsilyl)amide produces the phthalonitrile **30**. In contrast to this, 3,6-dialkoxyphthalonitriles can be synthesized directly from 2,3-dicyanohydroquinone (**31**) via an *o*-alkylation reaction with numerous alkyl halides in acetone in the

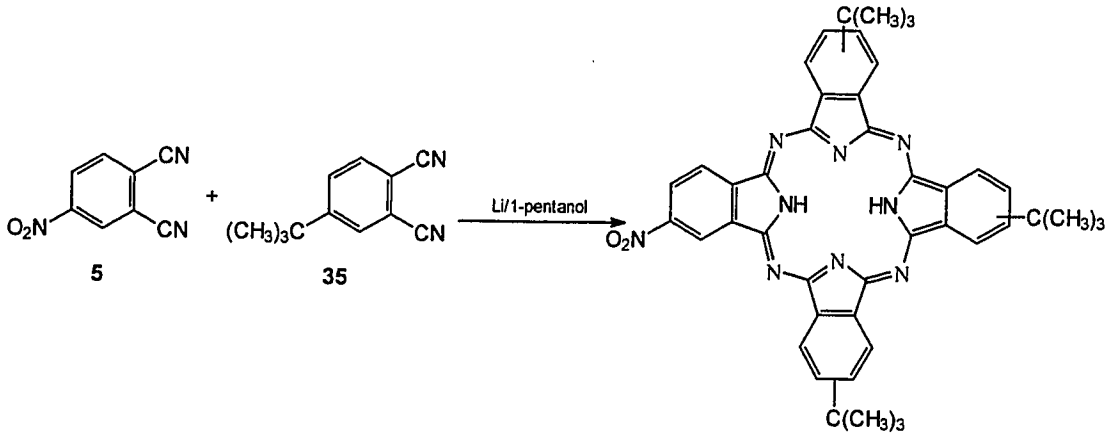
presence of K_2CO_3 to yield the 3,6-dialkoxyphthalonitrile **32**, (Scheme 7) [35]. Condensation of the phthalonitriles **30** and **32** in the presence of a metal salt produces the corresponding alkyl (**33**) or alkoxy (**34**) phthalocyanine.



Scheme 7. Synthesis of 1,4,8,11,15,18,22,25-octasubstituted phthalocyanines

Cross-Condensation Reactions

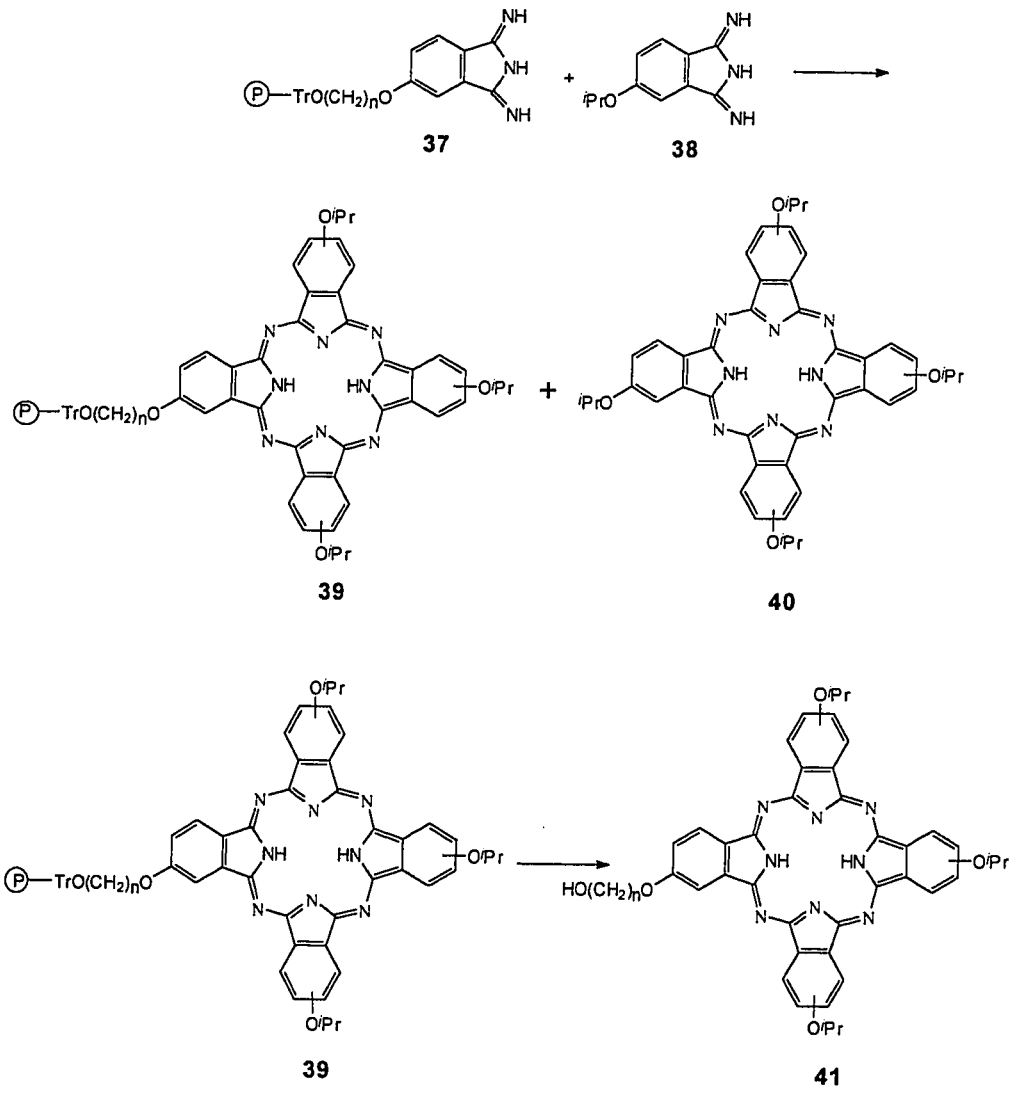
Non-centrosymmetric phthalocyanines are obtained when two different phthalonitriles (A and B) are reacted in a cross-condensation reaction. Statistical condensation is the most widely used strategy for synthesizing phthalocyanines consisting of three identical (A) and one different (B) isoindole units. In this strategy, as outlined in Scheme 8, one of the phthalonitriles is present in stoichiometric excess [36]. Thus in the condensation of 4-nitrophthalonitrile (**5**) with an excess of 4-*t*-butylphthalonitrile (**35**), the non-centrosymmetric phthalocyanine (**36**) was obtained along with a symmetric phthalocyanine from the self-condensation of **35**. However, since a difference in solubility between the two phthalocyanines exists, their separation was possible by chromatographic methods.



5 **35** **36**

Scheme 8. Synthesis of A_3B substituted phthalocyanines

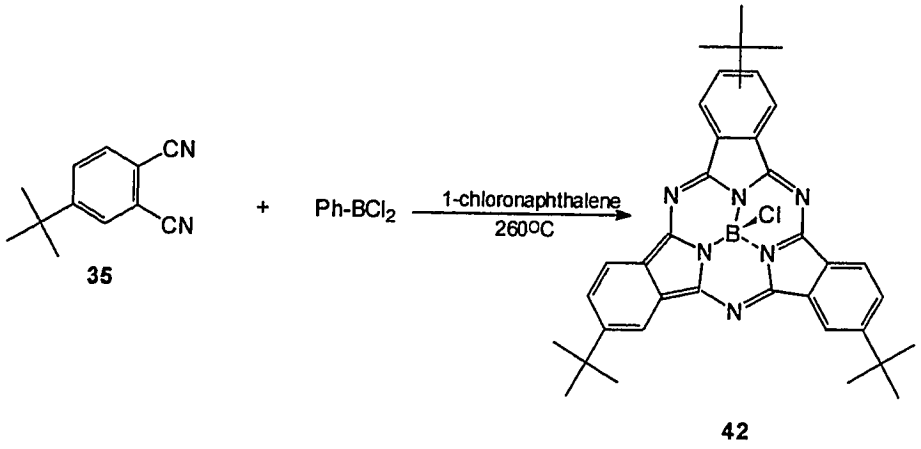
An alternative approach to the synthesis of unsymmetric A_3B substituted phthalocyanines involves the use of a polymer support. In this method an



Scheme 9. Synthesis of an A_3B substituted phthalocyanine using a polymer support method

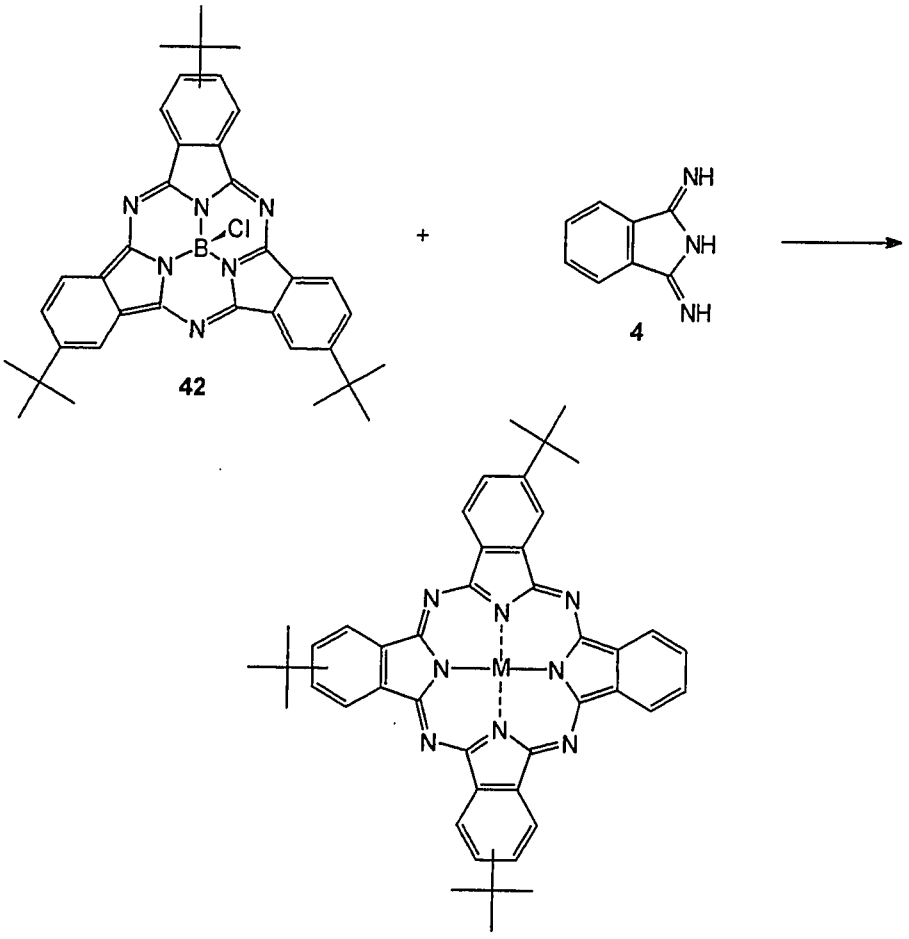
appropriately substituted phthalonitrile or 1,3-diiminoisoindoline is attached to an insoluble polymer support (**37**). The polymer-bound **37** is treated with a large excess of a second soluble diiminoisoindoline (**38**) to give the polymer-bound phthalocyanine **39**, (Scheme 9) [17, 37, 38]. Isolation of the A_3B substituted phthalocyanine involves washing the polymer to remove the symmetrically substituted phthalocyanine (**40**); this is followed by acid cleavage of the phthalocyanine from the polymer to yield the unsymmetrical Pc (**41**). A limitation of this method is that only phthalonitriles possessing appropriate functional groups such as hydroxy groups can be attached to the polymer support [39].

Another method for the preparation of unsymmetrically A_3B substituted Pcs involves ring expansion of subphthalocyanines (**42**) (Sub Pcs). These macrocyclic complexes, which are the lowest homologues of phthalocyanines, are composed of three isoindole units with boron as the central atom [40]. Synthesis of these cone-shaped molecules involves the reaction of a phthalonitrile, such as *t*-butylphthalonitrile (**35**), with a boron halide to yield the sub Pc **42**, Scheme 10.



Scheme 10. Synthesis of a subphthalocyanine

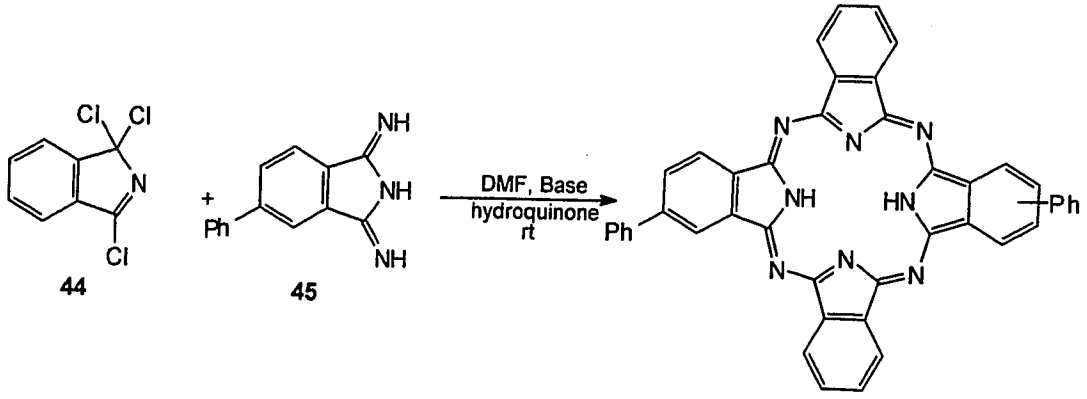
Subphthalocyanines are structurally strained and unstable compounds; it should be noted that it is these characteristics that allow them to be used in ring-expansion reactions [41]. In the presence of diiminoisoindoline (**4**) the subPc is readily cleaved and the diiminoisoindoline unit is incorporated into its framework to form the unsymmetric A_3B substituted Pc (**43**), Scheme 11 [40].



Scheme 11. Synthesis of an A_3B phthalocyanine by ring expansion of a subPc

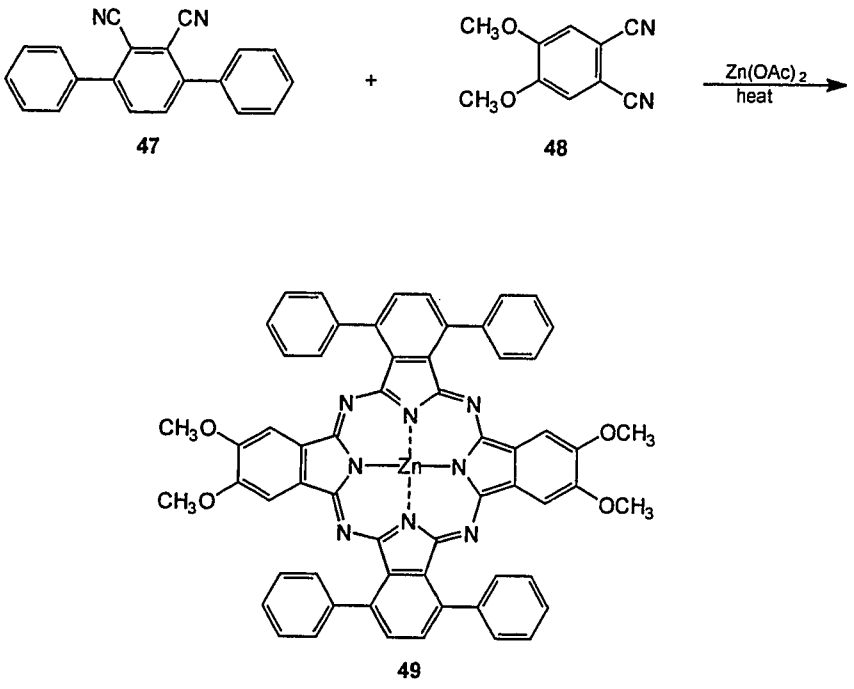
Recently it has been shown that this synthetic strategy produces phthalocyanines other than the desired A_3B substituted Pc. It is thought that the incorporation of the diiminoisoindoline unit proceeds through partial or total fragmentation of the subphthalocyanine ring.followed by statistical ring closure of the fragments, giving rise to a mixture of all possible phthalocyanines [39].

The selective synthesis of ABAB substituted phthalocyanines of D_2h symmetry was first reported in two patents [42]. In general, this procedure involves the reaction of 1,3,3-trichloroisoindolenine (**44**) with a diiminoisoindoline, such as 5-phenyl-1,3-diiminoisoindoline (**45**), in the presence of an acid acceptor and a reducing agent, Scheme 12. The major product of this reaction is 2,16- and 2,17-diphenylphthalocyanine (**46**), however trace amounts of trisubstituted phthalocyanines are also observed. It is important to note that, in this synthesis, formation of the AABB substituted phthalocyanine is avoided since the self-condensation of **45** does not occur at room temperature and the self-condensation of **44** is unlikely [2].



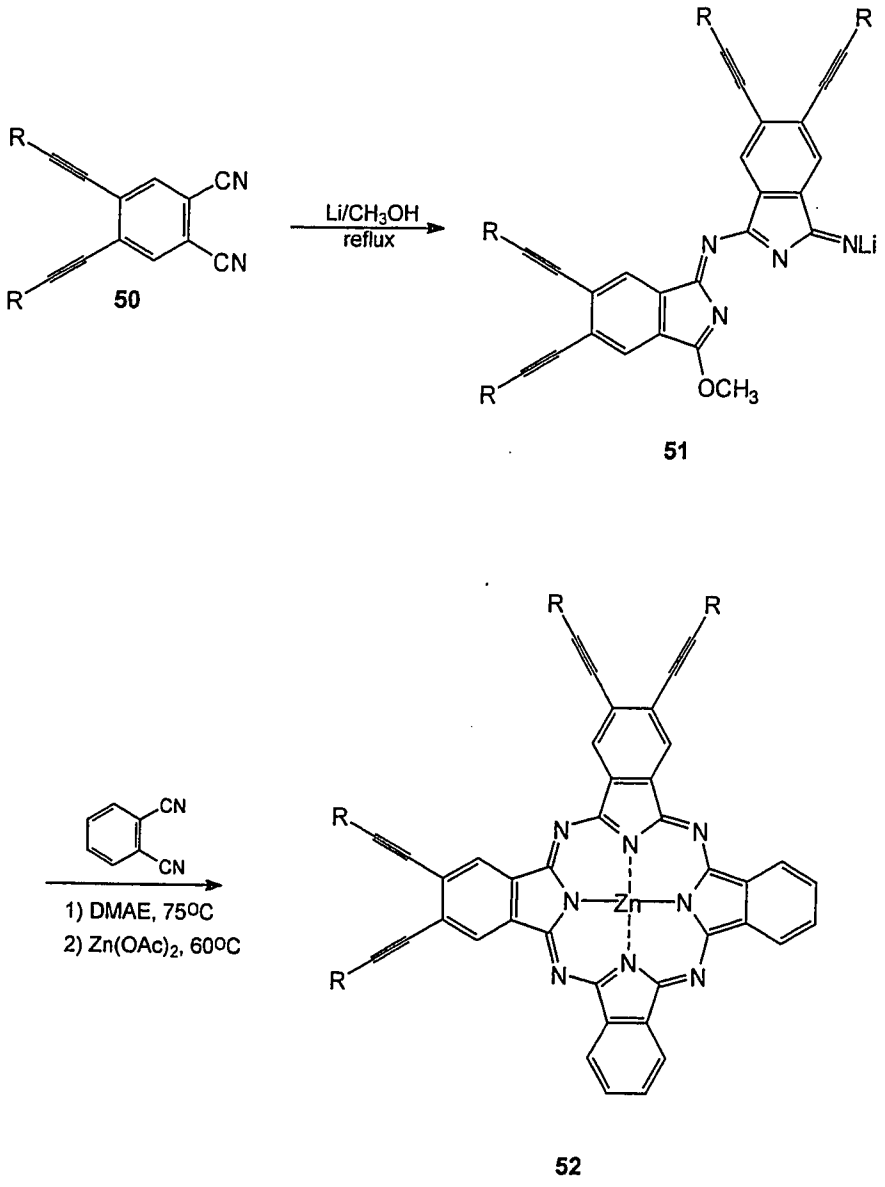
Scheme 12. Synthesis of an ABAB substituted phthalocyanine

An alternative strategy for the synthesis of ABAB substituted phthalocyanines takes advantage of steric interactions between bulky phthalonitriles in order to prevent the formation of any AABB substituted phthalocyanine [43, 44]. Thus, in the cross-condensation reaction of 3,6-diphenylphthalonitrile (**47**) with three equivalents of 4,5-dimethoxyphthalonitrile (**48**) (Scheme 13), formation of AABB substituted phthalocyanine is prevented due to steric hindrance between the bulky phenyl groups. Only the ABAB substituted isomer (**49**) and trace amounts of 16,17-dimethoxy-1,4,8,11,15,18-hexaphenyl- phthalocyanine were obtained [44].



Scheme 13. A steric constraint approach toward the synthesis of an ABAB substituted phthalocyanine

A synthetic method for the preparation of AABB substituted phthalocyanine involves treating a substituted phthalonitrile (**50**) with lithium methoxide to form a "half-Pc" intermediate (**51**), Scheme 14 [45].

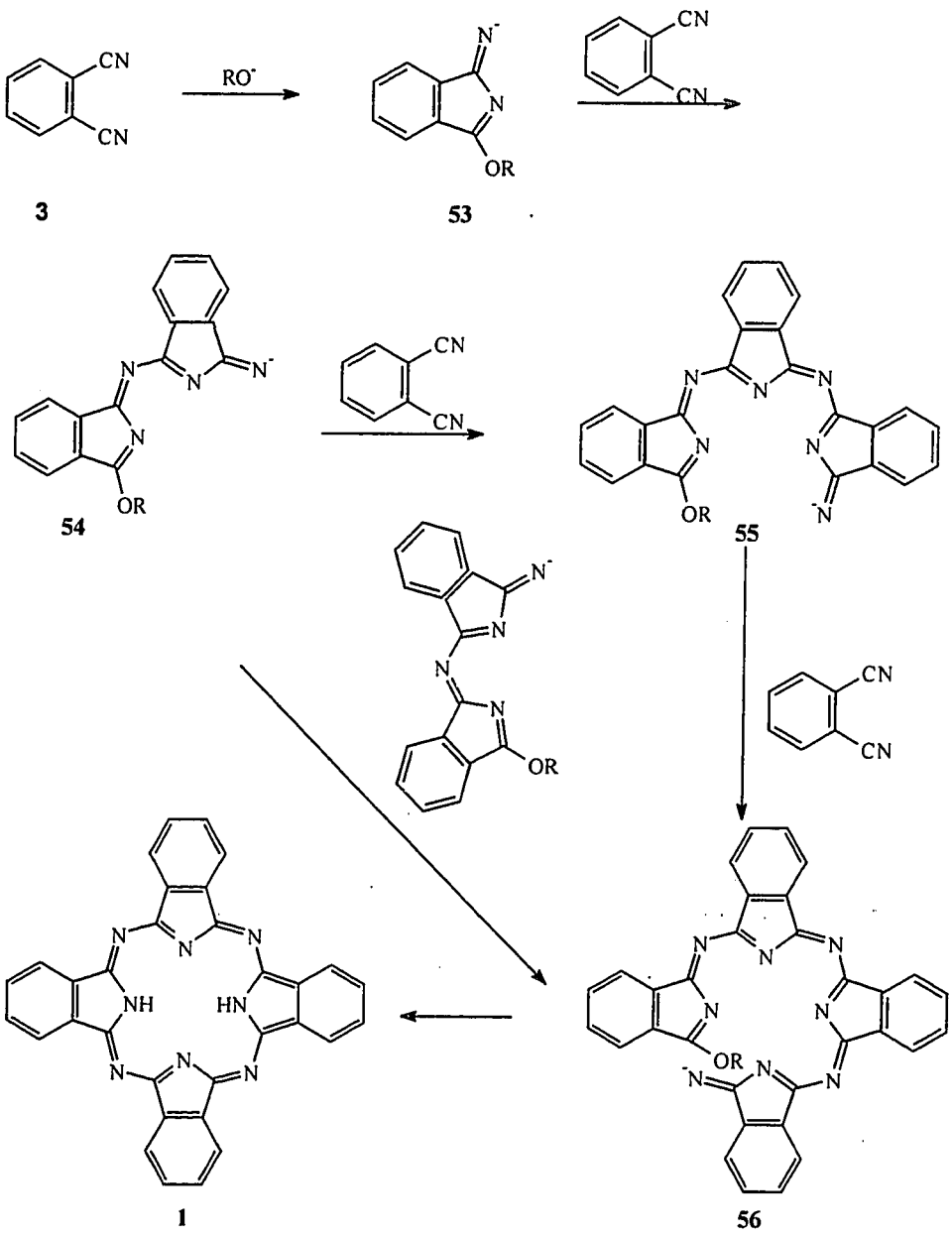


Scheme 14. Synthesis of an AABB substituted phthalocyanine

Along with the formation of the dimeric intermediate, small amounts of monomeric and trimeric intermediates are also observed. Subsequent treatment of this mixture of intermediates with an excess of phthalonitrile (**3**) yields mostly the AABB substituted phthalocyanine (**52**), along with small amounts of other Pcs, Scheme 14. Formation of the ABAB substituted phthalocyanine is not observed using this method [45].

Mechanism of Phthalocyanine Formation

Phthalocyanine formation usually proceeds in one synthetic step through complex reaction pathways involving formation of reactive intermediates [40]. Due to the different reaction conditions used in the synthesis of these compounds, a detailed comprehension of the mechanism has been difficult to obtain [40]. However, it has been proposed that formation of phthalocyanine under lithium alkoxide conditions occurs by the mechanism shown in Scheme 15 [46]. According to this mechanism, the alkoxide attacks one of the cyano groups of the phthalonitrile (**3**) to form a monomeric intermediate (**53**), which subsequently reacts with another phthalonitrile to form a half-Pc intermediate (**54**). The half-Pc intermediate can react with a second half-Pc intermediate to



Scheme 15. Mechanism of phthalocyanines formation

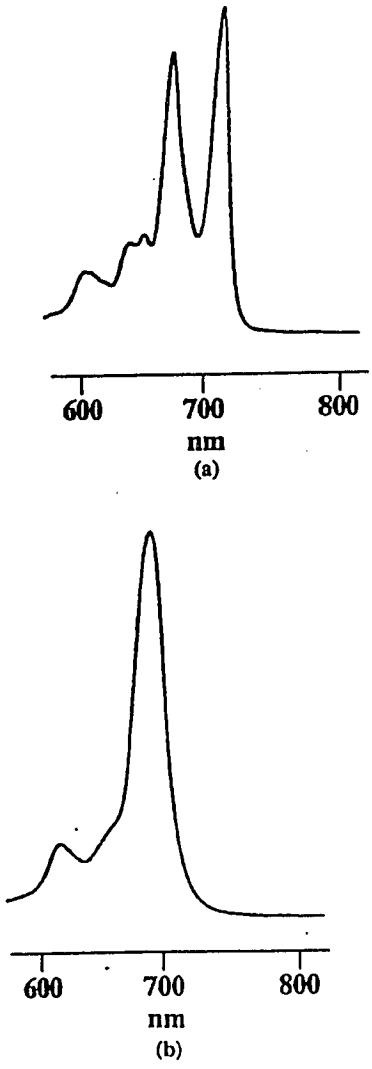
form Pc, or it can sequentially react with phthalonitrile to form a trimeric intermediate (**55**) then a tetrameric intermediate (**56**) intermediate which cyclizes to give phthalocyanine. In the cyclization step, a two-electron reduction of the macrocycle is required to obtain the final 18π electron aromatic system. This is achieved by the oxidation of the alcohol, which initiated the cyclization process; to an aldehyde.

Electronic Spectra of Phthalocyanines

The application of phthalocyanines as dyes and pigments is due to their extremely strong absorption of light to give intense blue or green colors. Typical visible absorption spectra for metal-free and metallophthalocyanine in solution are shown in Figure 3. As a result of the large, extended π-conjugation of the Pc ring, the phthalocyanines exhibit strong absorptions between 670 and 690 nm, which is referred to as the Q band. It is this absorption that is responsible for the characteristic intense blue and blue-green color of phthalocyanines. In addition to this, there are weak absorption bands at around 600 nm which are vibrational overtones of the Q-band. Also, there is another strong absorption in the ultra-violet (UV) region between 320 and 370 nm that is referred to as the B-band or Soret Band. The symmetry of the phthalocyanine macrocycle determines the

structure of the Q-band. In the case of the metallophthalocyanines, which belong to the D_{4h} point group, a single absorption is observed in the Q-band

Figure 3. UV-Visible spectra of the Q-band region of metal-free and metallated phthalocyanines [3]



region. In contrast to this, metal-free phthalocyanines, which belong to the D_{2h} point group, display a split Q-band [3].

Non-linear Optics

Non-linear optics is the study of phenomena that occur as a consequence of the modification of the optical properties of a material system by the presence of light [47]. Typically, only laser light is sufficiently intense to modify the optical properties of a material system. Non-linear optical phenomena are "non-linear" in the sense that they occur when the response of a material system to an applied optical field depends in a non-linear manner upon the strength of the optical field [47].

When light passes through a medium, it induces an oscillating polarization (P) which is usually regarded as being linearly proportional to the light's electric field (E) and is defined by equation (1), in which ε_0 is the permittivity of free space and χ is the polarizability of the medium:

$$P=\varepsilon_0\chi E \qquad (1)$$

However, for higher light intensities, such as those obtained from laser light sources, deviation from this linear relationship occurs and higher powers of the electric field become important:

$$P=\varepsilon_0(\chi^{(1)}E+\chi^{(2)}E^2+\chi^{(3)}E^3\ldots) \quad (2)$$

The terms $\chi^{(2)}$ and $\chi^{(3)}$ are known as the second-order and third-order hyperpolarizabilities, respectively. A property that arises from materials possessing large second-order hyperpolarizabilities is frequency doubling of the incident light. Similarly, materials that possess large third-order hyperpolarizabilities have the ability to triple the frequency of the incident light [3].

For an organic material to exhibit large non-linear hyperpolarizabilities, it should possess a molecular structure with a large polarizable π-system. In order to possess significant values of second-order molecular hyperpolarizabilities, a permanent molecular dipole moment must be associated with the π-system [49-51]. In contrast to this, phthalocyanines that do not possess a permanent molecular dipole are of interest as third-order non-linear optical materials.

Another non-linear optical effect, optical limiting, is useful for the construction of optical filters to protect eyes against intense light sources such as laser weapons. Phthalocyanines are among the most promising organic materials for use as optical limiters [51].

Objective

Organic materials that possess a delocalized π-electron system have attracted a great deal of research interest in the field of nonlinear optics. In particular, phthalocyanines have been extensively studied, since these molecules have a highly conjugated π-electron macrocycle and they provide tremendous architectural flexibility. A promising application of phthalocyanines in the field of nonlinear optics is its use as an optical limiting material that will protect against particular types of lasers. This application is possible since the light absorbance of phthalocyanines over the range of 670-850 nm can be fine-tuned by varying the position, number and types of substitutents on the periphery of the macrocyle. However, in order to realize the full potential of phthalocyanines as optical limiters, or in any other application, the problem of their low solubility has to be addressed. To overcome this problem, the neopentoxy group will be used as a bulky substituent to enhance solubility.

A series containing octa- and hexadecaneopentoxy- substituted phthalocyanines will be synthesized and the Q-band shift of these highly soluble compounds will be determined. Further red-shifting of the Q-band absorption can be achieved by the addition of π-donating substitutents to the periphery of the phthalocyanine macrocycle. This phenomenon is enhanced as the π–donating effect of the substituent increases. Thus, further red-shifting of the Q-

band can be achieved by alkylamino and alkylthio substituents, but only a few examples of phthalocyanines with such substitution are known. A synthetic route toward the preparation of tetrasubstituted phthalonitriles, consisting of amino-thiol and amino-alkoxy substituents, will be developed. Subsequently, these novel phthalonitriles will be used in cross-condensation reactions to give non-centrosymmetric phthalocyanines, which should display second-order nonlinear optical responses. Furthermore, the steric interactions of adjacent bulky groups will be examined by variable temperature ^{1}H-NMR spectroscopy and their thermokinetic parameters will be determined.

RESULTS AND DISCUSSION

Synthesis of Novel Phthalonitriles and Phthalocyanines

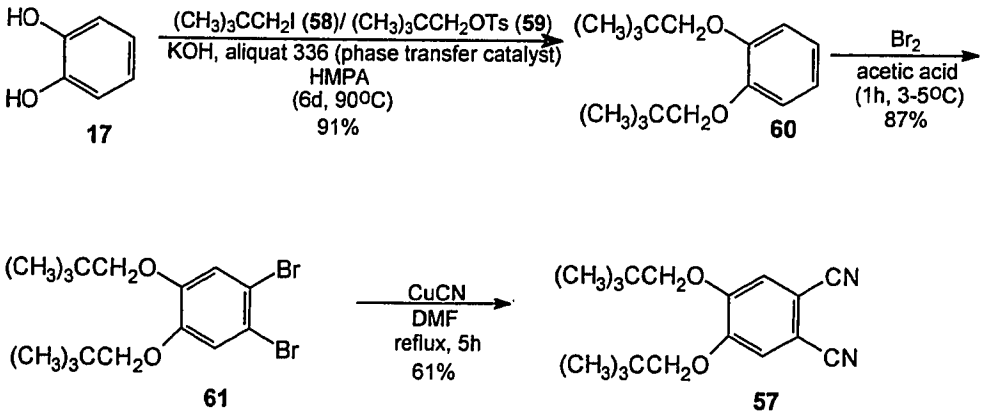
Synthesis of 4,5-dineopentoxyphthalonitrile (**57**) and phthalocyanines (**62** and **63**) derived from (**57**)

The starting phthalonitrile (**57**) was prepared via a 3-step reaction sequence, beginning with the *O*-alkylation of catechol (Scheme 16). These alkylations can generally be performed by reacting the disodium salt of catechol with an alkyl bromide via an S_N2 mechanism [52]. Synthesis of dineopentoxy catechol however, is not as straightforward since the steric bulk of the tert-butyl group severely hinders the electrophilic site to back-side attack [53-55]. Another difficulty associated with neopentyl systems reacting via the S_N2 mechanism is that they are known to frequently rearrange to the *tert*-amyl system [55]. It has been found however, that neopentyl tosylate can undergo nucleophilic displacement without rearrangement when treated with various nucleophiles in hexamethylphosphoramide (HMPA) solvent [55]. It has been proposed that the role of HMPA must be to strongly solvate the cation leaving the anion to act as a free nucleophile unencumbered by ion pairing.

Thus, the *O*-alkylation of catechol (**17**) was successfully performed using both neopentyl iodide (**58**) or neopentyl tosylate (**59**) [56] in HMPA to yield 1,2-dineopentoxybenzene (**60**). Both of these reactions produced the desired product in high yields but long reaction times were required to drive the reaction

to completion. It is probable that steric hindrance resulting from the adjacent placement of the two neopentyl groups added to the long reaction time.

The second step in Scheme 16 involved the bromination of **60** in acetic acid at 3-5°C. The addition of two molar equivalents of bromine to **60**, in the presence of an iodine crystal to induce bromination, afforded 1,2-dibromo-4,5-dineopentoxybenzene (**61**) in an 87% yield. Usually, in these types of reactions, the tribrominated compound is often obtained as a side product. However, probably due to the steric hindrance of the bulky neopentoxy groups, this side-product was not observed.



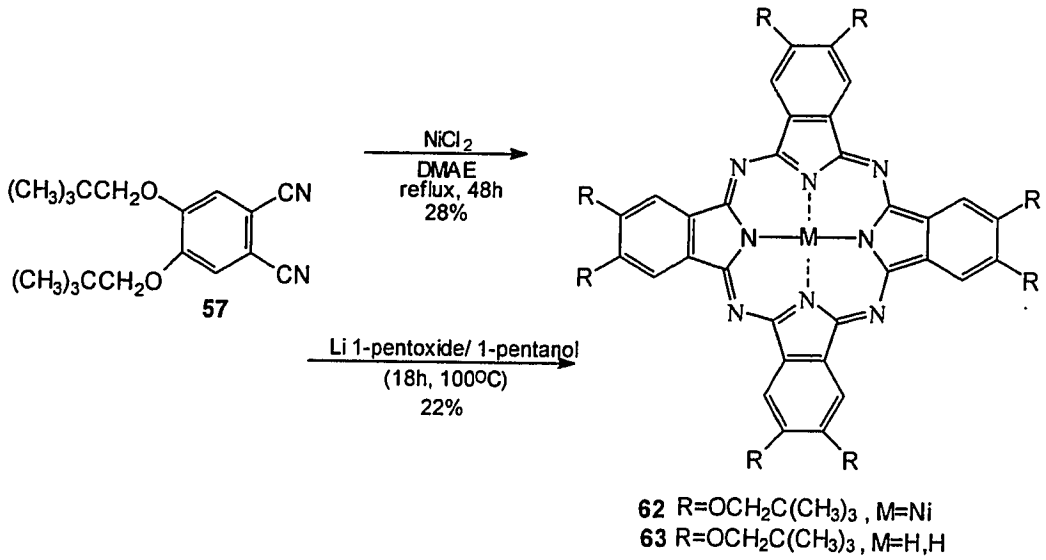
Scheme 16. Synthesis of 4,5-dineopentoxyphthalonitrile (**57**)

Conversion of compound **61** to the corresponding phthalonitrile (**57**) was carried out by the Rosenmund-von Braun reaction [57]. An excess of CuCN reacted with the dibromo compound **61** in refluxing DMF for 5 h to give 4,5-

dineopentoxyphthalonitrile (**57**) in a 61% yield. Longer reaction times decreased the yield of product due to the formation of 2,3,9,10,16,17,23,24-octaneopentoxyPc Cu.

Subsequent condensation of the phthalonitrile **57** in the presence of $NiCl_2$ in refluxing DMAE (Scheme 17) afforded 2,3,9,10,16,17,23,24-octaneopentoxyphthalocyanine nickel (II) (**62**). This green solid was highly soluble in many of the common organic solvents such as benzene, toluene, cyclohexane, methylene chloride, chloroform, tetrahydrofuran and acetone. Its purification was accomplished by flash silica gel column chromatography using 80% toluene/ 20% hexane as the eluting solvent. Further purification involved reprecipitation from toluene/hexane to give **62** in an overall yield of 28%. The ^{1}H-NMR spectrum (Figure 4) displays the expected downfield aromatic protons at 9 ppm along with signals for the OCH_2 and t-butyl groups of the neopentoxy moieties are present at 3.8 and 1.3 ppm respectively.

Condensation of the phthalonitrile **57** to the corresponding metal free phthalocyanine (**63**) was accomplished by treatment with lithium 1-pentoxide in 1-pentanol at 100°C (Scheme 17). Upon acidic work up, a dark green solid was obtained which was chromatographed on a flash silica gel column using 5% hexane/ 95% toluene as eluent. Final purification involved reprecipitation from toluene/ethanol to give the Pc in an overall yield of 22%.



Scheme 17. Synthesis of 2,3,9,10,16,17,23,24-octaneopentoxyphthalocyanines (**62**, **63**)

The UV-Visible spectrum of **63**, taken in toluene, showed a split Q band absorption typical of a metal-free phthalocyanine. The room temperature ^{1}H-NMR spectrum, however, did not display the two highly shielded internal protons, which usually appear at approximately -1 ppm. At 330 K however, the internal protons appeared as a broad signal at -0.71 ppm. This phenomenon can be explained by a N-H tautomerization. At room temperature, slow tautomerization results in the appearance of a broad signal, which is lost in the baseline. At elevated temperatures, N-H tautomerization occurs at a faster rate and an averaged signal is observed [58-60].

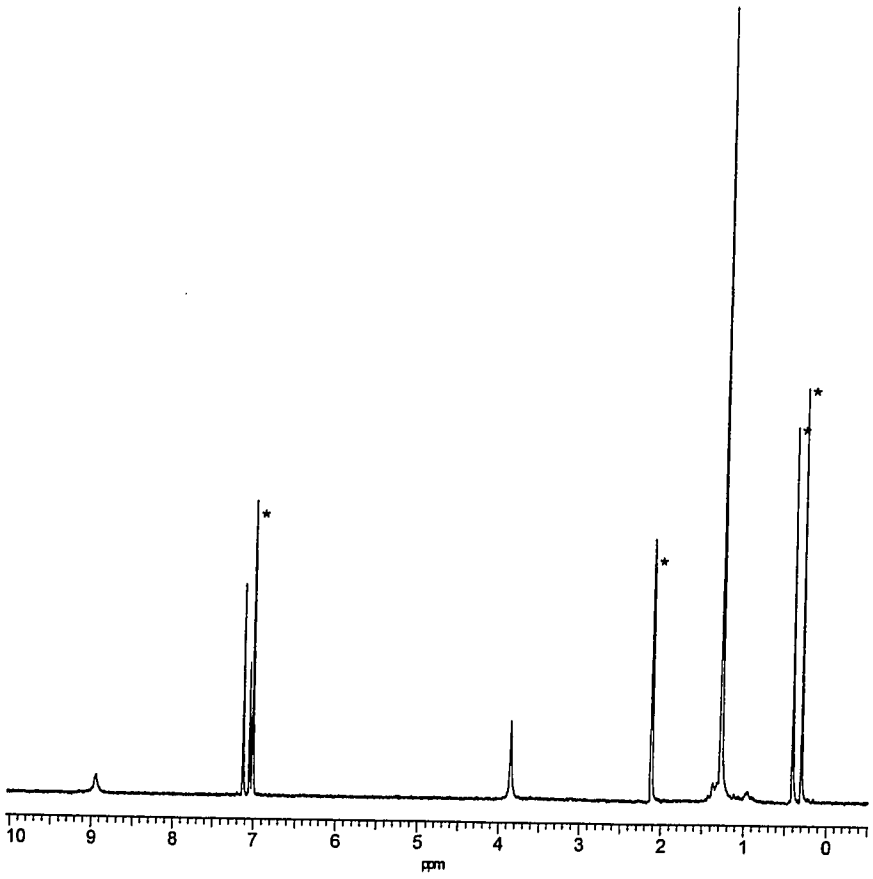
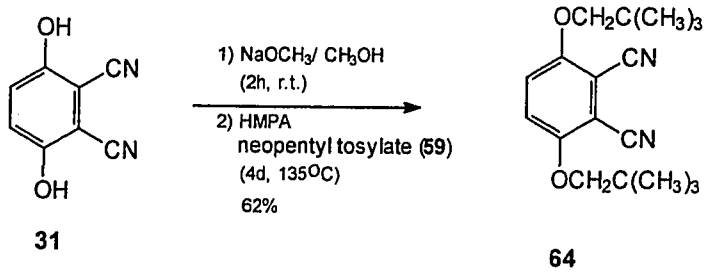


Figure 4. The ^{1}H-NMR spectrum of **62** in toluene-d_8
(solvent peaks have been marked with an asterisk (*))

Synthesis of 3,6-dineopentoxyphthalonitrile (**64**) and its corresponding phthalocyanine (**65**)

The synthesis of 3,6-dineopentoxyphthalonitrile (**64**) was carried out by the *O*-alkylation of commercially available 2,3-dicyano-1,4-hydroquinone (**31**) (Scheme 18). The hydroquinone was deprotonated using sodium methoxide in

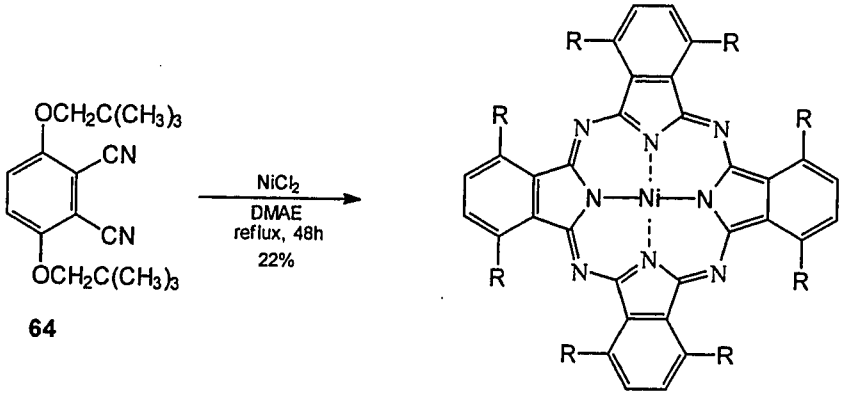
methanol at room temperature, and then reacted with neopentyl tosylate (**59**) in HMPA at 135°C to afford **64** as a white solid in 62% yield.



Scheme 18. Synthesis of 3,6-dineopentoxyphthalonitrile (**64**)

Condensation of **64** in the presence of $NiCl_2$ in refluxing DMAE afforded 1,4,8,11,15,18,22,25-octaneopentoxyphthalocyanine nickel (II) (**65**) (Scheme 18). Purification involved chromatography on a flash silica gel column using 50% hexane/ 50% toluene as eluents. This was followed by reprecipitation from toluene/ hexane to give the nickel phthalocyanine in a 22% yield. In comparison with phthalocyanine **62**, the structural isomer **65** displayed a higher degree of solubility in many of the common organic solvents. This was evident in the acquisition of ^{13}C-NMR spectra. In the case of compound **65**, a well-resolved spectrum was obtained through an overnight acquisition experiment (Figure 5). In contrast to this, the sample of compound **62** partially precipitated in toluene-d_8 during the experiment and, consequently, a satisfactory ^{13}C-NMR spectrum could not be obtained. In general, ^{13}C-NMR spectra of phthalocyanines are not

recorded, due to their highly insoluble nature. The ^{1}H-NMR spectrum of **65** displayed an upfield aromatic signal at 7.40 ppm relative to the aromatic signal of **62**. This is due to the aromatic ring current of the phthalocyanine macrocycle, which causes downfield shifts of the protons in the 1,4,8,11,15,18,22,25-positions relative to those in the 2,3,9,10,16,17,23,24-positions. Also, the protons of the substituents in the 1,4,8,11,15,18,22,25-positions are closer to the macrocylic core than those in the 2,3,9,10,16,17,23,24-positions and are therefore more affected by the ring current, which causes downfield shifts.



64

65 R=$OCH_2C(CH_3)_3$

Scheme 19. Synthesis of 1,4,8,11,15,18,22,25-octaneopentoxyphthalocyanine nickel (**65**)

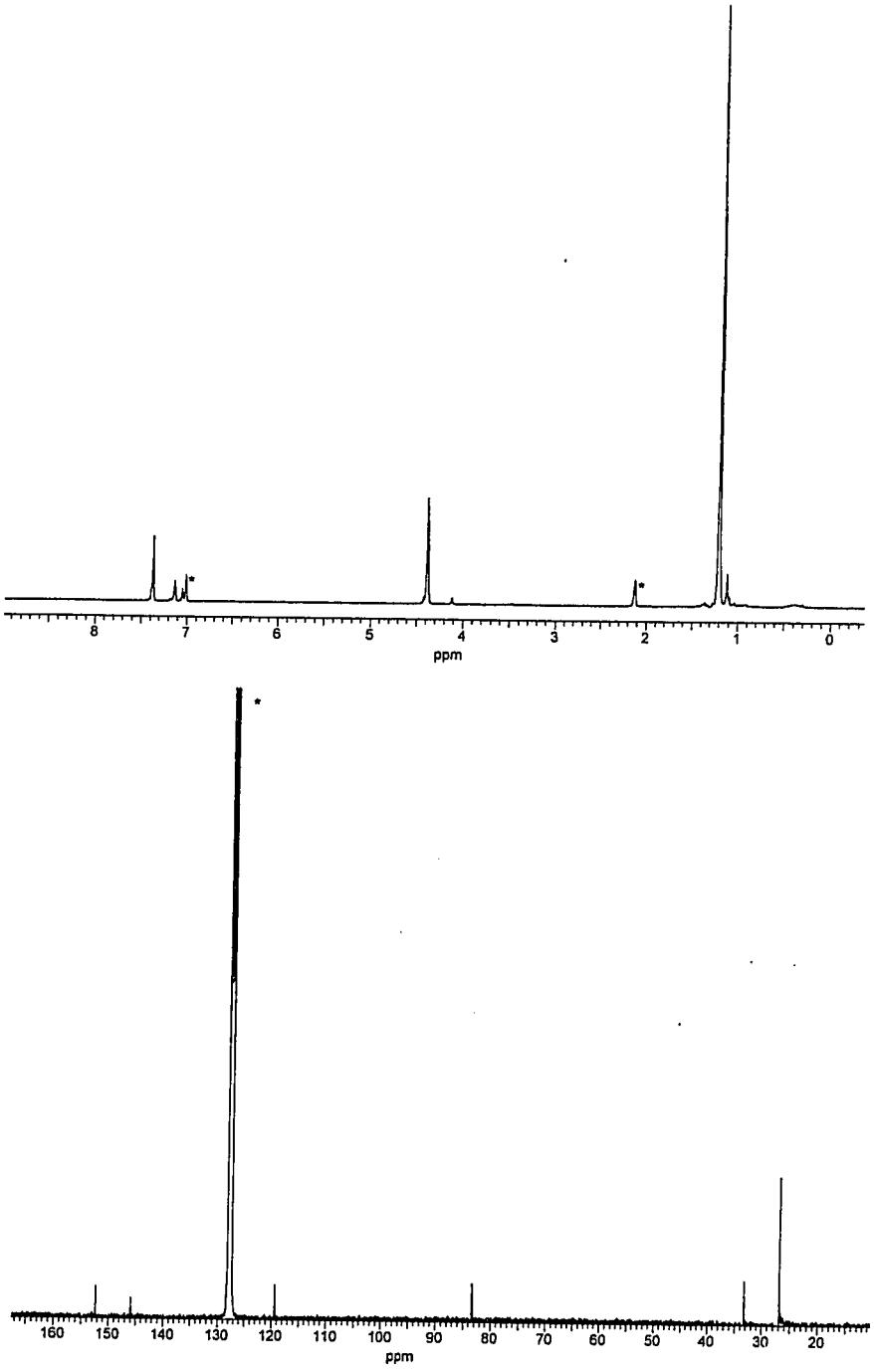
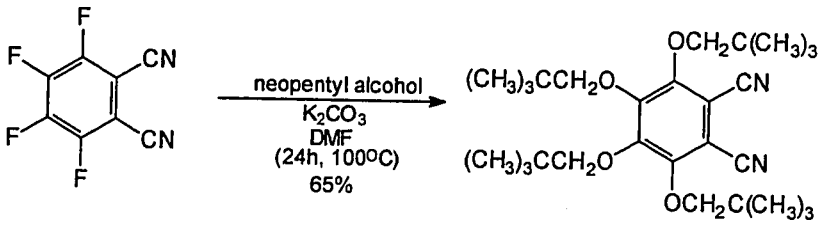


Figure 5. The ^{1}H-(toluene-d_8) and ^{13}C-(benzene-d_6) NMR spectra of **65** (solvent peaks have been marked with an asterisk (*))

Synthesis of 3,4,5,6-tetraneopentoxyphthalonitrile (**67**) and its corresponding NiPc (**68**)

Conversion of 3,4,5,6-tetrafluorophthalonitrile (**66**) to the corresponding tetraalkoxy-substituted phthalonitrile was performed via a nucleophilic aromatic substitution reaction. Commercially available **66** reacted with neopentyl alcohol in DMF at 100°C in the presence of potassium carbonate to give 3,4,5,6-tetraneopentoxyphthalonitrile (**67**) in 65% yield (Scheme 20). Incomplete substitution of the fluoro groups gave an inseparable mixture of tri- and tetra-substituted products. Thus, in order to drive the reaction to completion, long reaction times and a large excess of neopentyl alcohol and base were necessary.

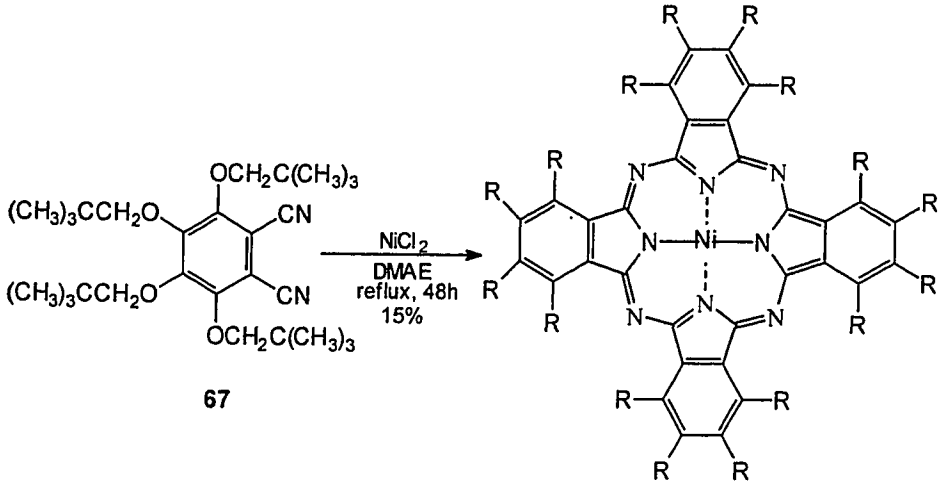


66 **67**

Scheme 20. Synthesis of 3,4,5,6-tetraneopentoxyphthalonitrile (**67**)

Condensation of the tetraneopentoxyphthalonitrile **67** to the corresponding phthalocyanine was attempted using several methods. Initially, in an attempt to synthesize metal-free phthalocyanine, **67** was heated in a lithium 1-octanolate/ 1-octanol solution at 100°C for 48h. Reaction probes taken of the resulting dark brown mixture at various time intervals did not reveal Q-band absorption peaks corresponding to Li_2Pc. Alternatively, a method involving the formation of diminoisoindoline *in situ* and its subsequent condensation to metal free phthalocyanine was attempted. This involved heating **67** under reflux in DMAE with continuous addition of ammonia gas, but again, phthalocyanine formation was not observed, as determined by UV-Visible reaction probes.

Although only a limited amount of work has been done on tetrasubstituted phthalonitriles, they are known to condense to their corresponding nickel phthalocyanines [61, 62]. At this time, it was decided to condense **67** to its corresponding nickel phthalocyanine to determine if phthalocyanine formation is possible or if it is being prevented by the steric bulk of the neopentoxy substituents. This condensation was performed by refluxing **67** in DMAE in the presence of $NiCl_2$, as outlined in Scheme 21. UV-Visible reaction probes of this green mixture revealed a strong Q-band absorption. After work up, the resulting green solid was found to be highly soluble in many of the common organic solvents. Purification of this compound was accomplished by flash silica gel



67

68 R=$OCH_2C(CH_3)_3$

Scheme 21. Synthesis of 1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-hexadecaneopentoxyphthalocyanine nickel (**68**)

column chromatography using 75% hexane/ 25% toluene as eluents to give 1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-hexadecaneopentoxyphthalocyanine nickel (II) (**68**) in a 15% yield.

The high degree of solubility of this compound permitted its full characterization; the ^{1}H-NMR spectrum is shown in Figure 6. The room temperature ^{1}H-NMR spectrum revealed a singlet in the OCH_2 region (2H) and two singlets in the t-butyl region (9H, 9H). However, as the temperature was increased above room temperature a new OCH_2 signal appeared and sharpened. It appears that the neopentoxy groups are experiencing hindered

rotation at room temperature; this phenomenon will be explored further in the variable temperature section.

Surprisingly, however, when **67** was treated with $Zn(OAc)_2$ in place of $NiCl_2$ phthalocyanine formation was not observed. In addition to this, it has been shown that not all tetrasubstituted phthalonitriles condense to their corresponding iron phthalocyanine. Since stable nickel salts of phthalocyanine intermediates have been isolated [63], it is possible that phthalocyanine intermediates have a stronger binding affinity to nickel over other metals thereby allowing nickel phthalocyanines to be synthesized.

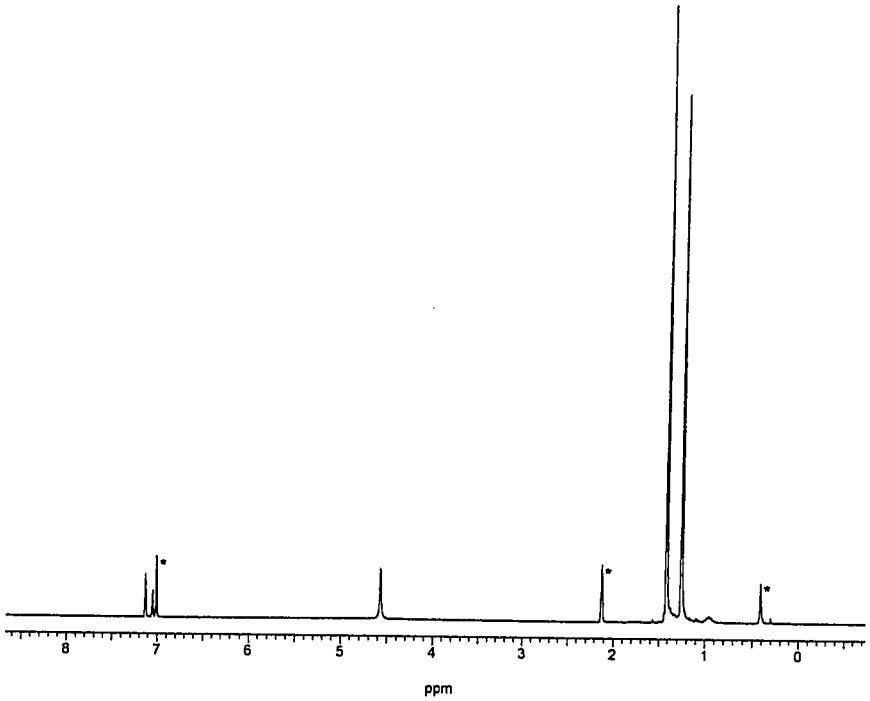


Figure 6. The ^{1}H-NMR spectrum of **68** in toluene-d_8 (solvent peaks have been marked with an asterisk (*))

The UV-Visible spectrum of **62** in toluene is displayed in Figure 7, similar spectra were obtained for **65** and **68**. An intense Q-band absorption was present in the visible region of the spectrum, which is typical for the π-π^* transition of the 18-π electron system in the macrocyclic core. A much less intense absorption around 300 mn was also observed, which would correspond to the Soret, or B-band absorption, also characteristic of a phthalocyanine. The addition of substituents to the periphery of the phthalocyanine macrocycle results in bathochromic shifts of the Q-band absorption. It has been shown that these shifts depend on the type, number and position of the substitutents. Substituents in the 1,4,8,11,15,18,22,25-positions generally cause a greater red shift of the Q-band absorption than do substituents in the 2,3,9,10,16,17,23,24-postions. This can be confirmed by comparing the Q-band signals of compounds **62**, **65** and **68**, which revealed a significant bathochromic shift as substituents were added at the 1,4,8,11,15,18,22,25-positions of the phthalocyanine macrocycle. For compound **62**, the Q-band absorption appeared at 672 nm, whereas for **65** and **68** it was shifted to 748 and 758 nm respectively (Table 1).

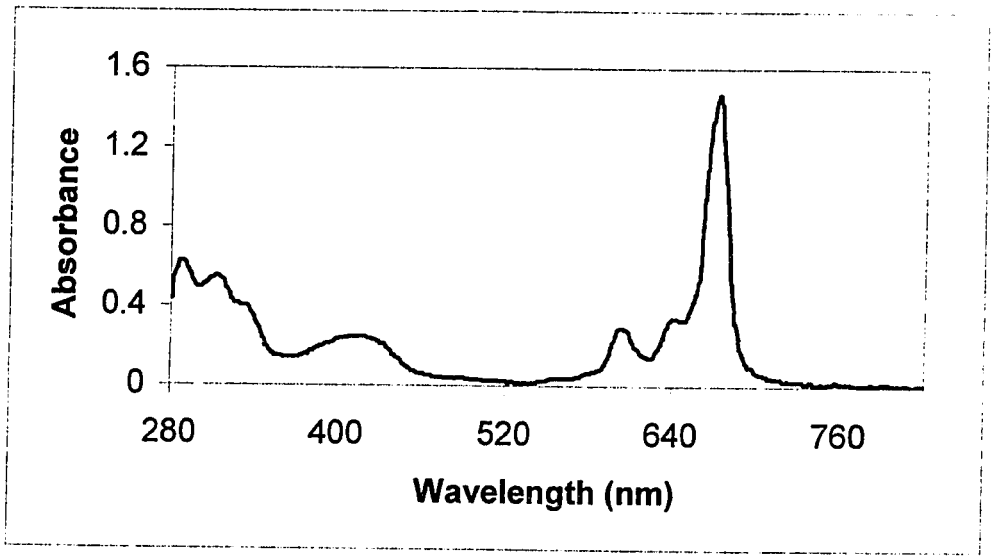


Figure 7. UV-Visible spectrum of **62** in toluene

Comparison of the Q-band signal of **62** and an unbranched isomer **69** (Table 1) did not reveal any significant differences. However, in the case of the **65** and **68**, bathochromic shifts were observed due to the degree of branching on the alkoxy substitutents. As the degree of branching increased, the Q-band signal was shifted more to the red region of the spectrum. For the highly branched Pc **65**, the Q-band absorption appeared at 748 nm, whereas for its known unbranched isomer, **70**, it appeared at 735 nm. In addition to this, the hexadecaneopentoxy Pc (**68**) can be compared with known hexadecahexyl (**71**) and hexadeca(2-ethylhexyloxy) Pc (**72**), since varying the chain length of the substituents has little or no effect on the position of the Q-band signal. In this

case the Q-band appeared at 731 nm for the unbranched **71** and was shifted to 745 nm as the branching was increased in compound **72**. Further branching, as in the case **68**, resulted in the Q-band shifting to 758 nm. Higher degree of branching on the substituents increases their electron donating ability and this may be causing the Q-band absorption to shift further to the red.

Table 1. Q-band absorption data for neopentoxy and other alkoxy nickel phthalocyanines

Phthalocyanine	Solvent	λ_{max} (nm)
2,3,9,10,16,17,23,24-octaneopentoxyPc Ni (**62**)	Toluene	672
1,4,8,11,15,18,22,25-octaneopentoxyPc Ni (**65**)	Toluene	748
1,2,3,4,8,9,10,11,15,16,17,18, 22,23,24,25-Hexadecaneopentoxy Pc Ni (**68**)	Toluene	758
2,3,9,10,16,17,23,24-OctapentylPc Ni (**69**) [52]	CH_2Cl_2	675
1,4,8,11,15,16,17,18-OctapentylPc Ni (**70**) [35]	Toluene	735
1,2,3,4,8,9,10,11,15,16,17,18, 22,23,24,25-Hexadeca hexyloxy Pc Ni (**71**) [61]	CH_2Cl_2	731
1,2,3,4,8,9,10,11,15,16,17,18, 22,23,24,25-Hexadeca(2-ethyl hexyloxy) Pc Ni (**72**) [61]	CH_2Cl_2	745

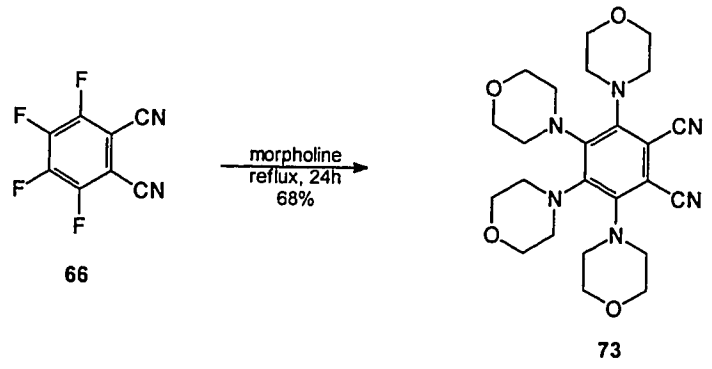
Branching of the alkoxy chains also resulted in a drastic increase in the melting point of the corresponding phthalocyanine. The melting point of the neopentoxyphthalocyanines **62**, **65** and **68** were found to be greater than 300°C.

In contrast to this, the unbranched Pcs **70** and **71** were found to melt at 198-200°C and 81-82°C respectively [35, 61]. Phthalocyanines are more compact when they are substituted with neopentoxy groups in comparison to less branched substituents. This more compact structure causes them to pack better in the solid state and this results in an increase in the melting point.

Synthesis of Amino Substituted Phthalonitriles

The hexadecaneopentoxy substituted phthalocyanine **68** showed a Q-band absorption at 753 nm. Further red-shifting of the Q-band signal should be possible by replacing the alkoxy substituents with amino groups. Only a limited amount of work has been done on amino phthalocyanines, probably due to their low solubility and difficulties associated with their purification [64-67].

As previously determined by the reaction of 3,4,5,6-tetrafluorophthalonitrile (**66**) with neopentyl alcohol, as outlined in Scheme 20, a large excess of the alcohol is required for complete substitution. For this reason, in the reaction of **66** with morpholine, the amine served as both nucleophile and solvent. Despite using a large excess of the amine, this reaction performed at 80°C yielded a mixture of trimorpholinomonofluorophthalonitrile and 3,4,5,6-tetramorpholinophthalonitrile (**73**), as determined by EI-MS and ^{1}H-NMR spectroscopy. Increasing the temperature to that of refluxing morpholine for 24 h afforded only **73**, Scheme 22.



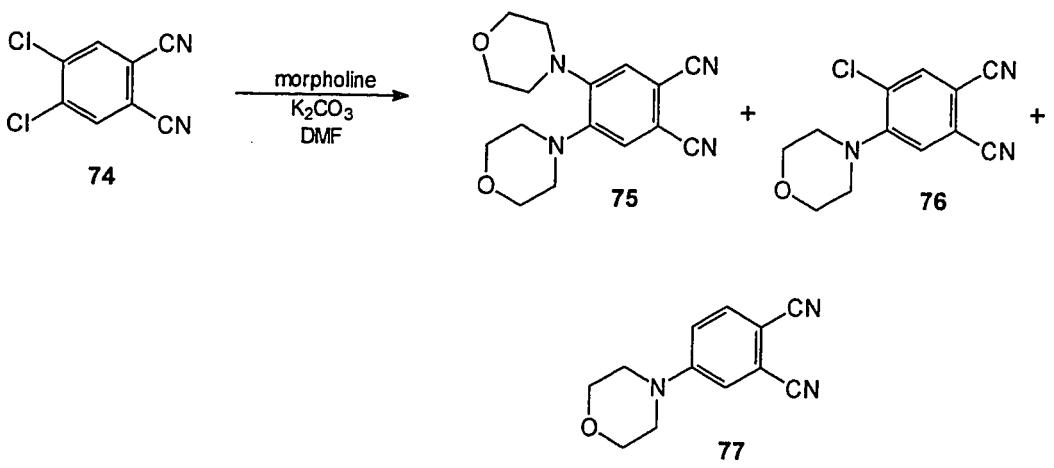
66 73

Scheme 22. Synthesis of 3,4,5,6-tetramorpholinophthalonitrile (**73**)

Subsequent condensation of **73** to the corresponding phthalocyanine was attempted using various methods. Initially, condensation was attempted under conditions similar to those used in the synthesis of hexadecaneopentoxy Pc, **68**. In contrast to the synthesis of **68**, heating the tetramorpholinophthalonitrile, **73**, for 48 h under reflux in DMAE in the presence of $NiCl_2$ did not result in any Pc formation as determined by UV-Visible reaction probes. In an alternative method, gaseous ammonia was continuously bubbled into a refluxing solution of **73** in DMAE. Unfortunately, UV-Visible probes of the reaction did not reveal any Q-band absorption. One final attempt at condensing this phthalonitrile was performed using lithium 1-octanolate in 1-octanol at 100°C but, again, reaction probes did not reveal any Q-band absorption.

At this time, attention was turned toward the synthesis of a 4,5-diaminophthalonitrile from the commercially available 4,5-dichlorophthalonitrile (**74**). It is known that replacement of the chloro substituents of **74** by phenols or

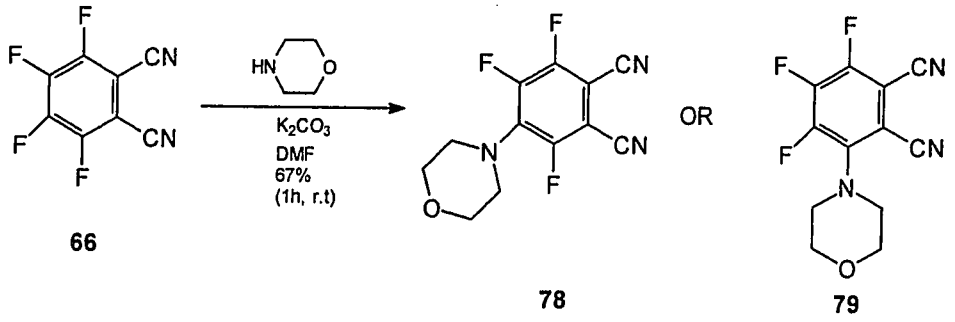
thiols can be readily achieved in DMF in the presence of K_2CO_3 [68]. Under similar reaction conditions, **74** reacted with an excess of morpholine in the presence of K_2CO_3 at 100°C, Scheme 23. Prolonged heating at this temperature afforded only trace amounts of 4,5-dimorpholinophthalonitrile (**75**). Side products that were obtained, also in trace amounts, are believed to be 4-chloro-5-morpholinophthalonitrile (**76**) and a dechlorination product, 4-morpholinophthalonitrile (**77**). The identification of these products was based on ^{1}H-NMR spectroscopy.



Scheme 23. Attempted synthesis of 4,5-dimorpholinophthalonitrile (**75**)

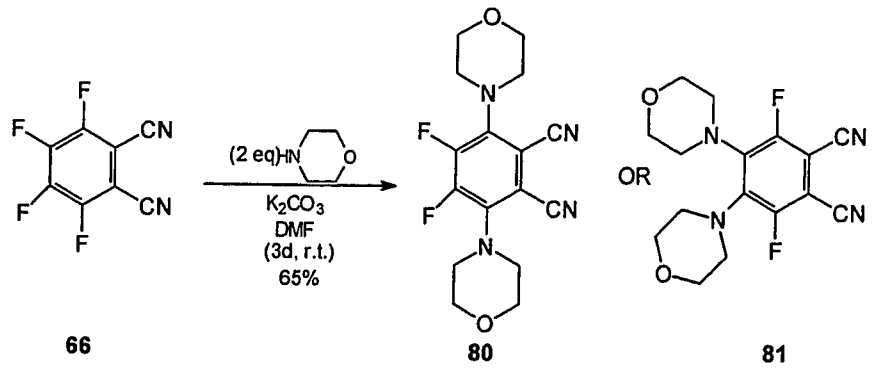
Since the synthesis of tetrasubstituted phthalonitriles containing amino substituents in the 4,5-positions was still desired, an alternative route starting from tetrafluorophthalonitrile was developed and is outlined in Scheme 24. It has been shown that in various nucleophilic aromatic reactions of polyfluorinated

compounds, selective replacement of the fluorines is possible [69, 70]. Specifically, treatment of tetrafluorophthalonitrile (**66**) with excess aqueous ammonia in dioxane afforded 4-amino-3,5,6-trifluorophthalonitrile in a 79% yield [71]. In a similar reaction, **66** was treated with a molar equivalent of morpholine in the presence of K_2CO_3 at room temperature, Scheme 24. This reaction proceeded quickly and gave only one product as determined by ^{1}H- and ^{19}F-NMR spectroscopy. The ^{1}H-NMR spectrum showed resonances corresponding to only one unique morpholine group, whereas ^{19}F-NMR showed resonances corresponding to three different fluoro substituents. Also, EI mass spectral analysis of this compound confirmed that only one of the fluorines had been replaced by morpholine. Based on the product assignment according to the literature, it was assumed that substitution occurred at the 4- position to give compound **78** rather than **79**. This assumption would be later confirmed.



Scheme 24. Synthesis of 3,5,6-trifluoro-4-morpholinophthalonitrile (**78**)

In a variation of the previous reaction, **66** was treated with one equivalent of morpholine and once formation of the monosubstituted compound was complete a second equivalent of each morpholine and K_2CO_3 were added, Scheme 25. The addition of a second morpholine group did not proceed as selectively as the addition of the first morpholine group. TLC of the reaction mixture revealed several close-running spots, however isolation of a pure compound was possible by crystallization from ethanol. The ^{1}H-NMR spectrum of the isolated compound displayed resonances corresponding to one unique morpholino substituent, whereas the ^{19}F-NMR spectrum displayed a single fluorine resonance. In addition to this, mass spectral analysis showed that the phthalonitrile was substituted with two morpholino and two fluoro substituents. Based on this information, the formation of either of the two symmetric products, **80** and **81**, was possible. An X-ray crystal structure, Figure 8, confirmed that the 3,6-difluoro-4,5-dimorpholinophthalonitrile (**81**) had been synthesized.



Scheme 25. Synthesis of 3,6-difluoro-4,5-dimorpholinophthalonitrile (**81**)

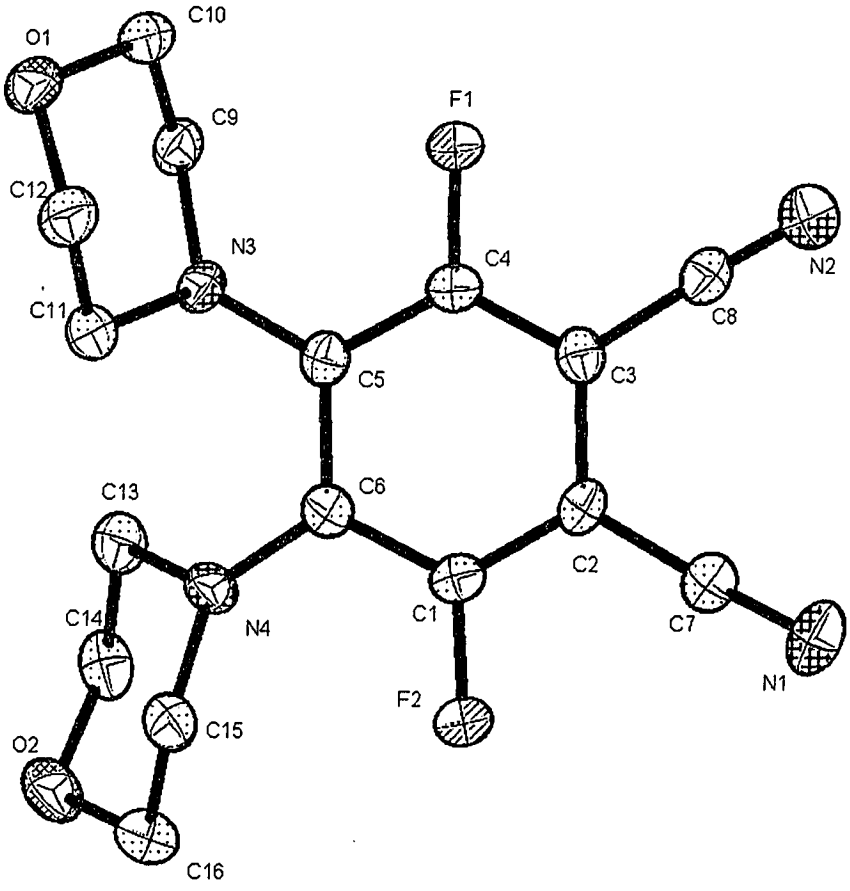
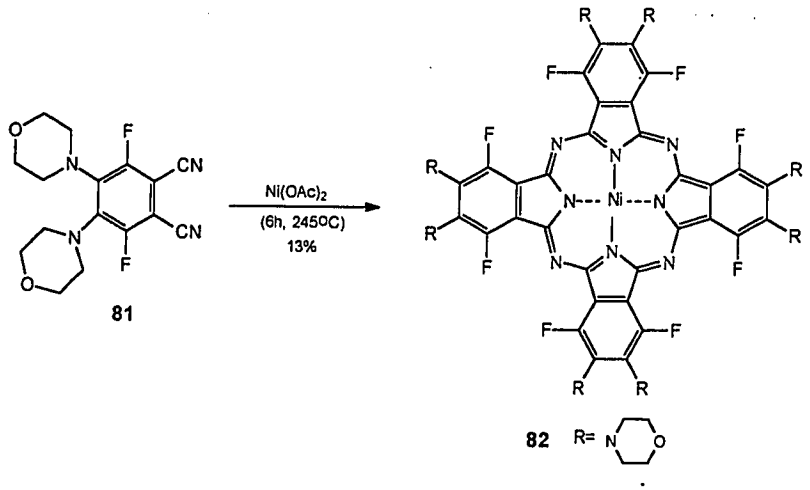


Figure 8. X-ray crystal structure of 3,6-difluoro-4,5-dimorpholinophthalonitrile (**81**) (crystallographic data is given in the appendix)

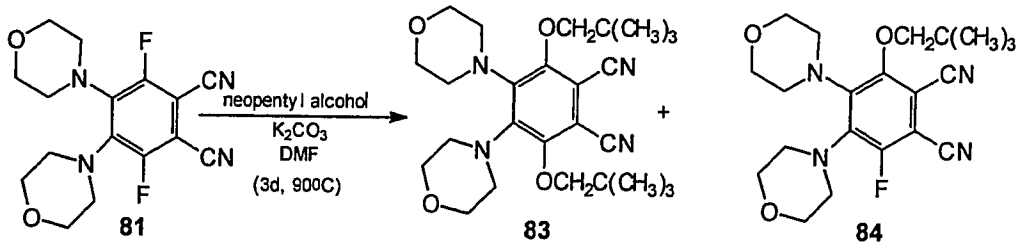
Synthesis of 1,4,8,11,15,18,22,25-octafluoro-2,3,9,10,16,17,23,24-octa-morpholinophthalocyanine nickel (II) (**82**)

Condensation of the dimorpholino compound **81** to the corresponding nickel phthalocyanine was carried out in the absence of a solvent, due to the possibility of the solvent displacing the remaining fluoro substituents [72, 73]. Compound **81** and a quarter molar equivalent of nickel acetate were finely ground using a mortar and pestle, transferred to a pressure bottle and heated at high temperature, Scheme 26. The resulting 1,4,8,11,15,18,22,25-octafluoro-2,3,9,10,16,17,23,24-ocatamorpholinophthalocyanine nickel (II) (**82**) was obtained as a dark green/black colored solid which was sparingly soluble in most organic solvents. It was, however, soluble in pyridine and DMSO, and this permitted its characterization by ^{1}H-NMR and ^{19}F-NMR spectroscopy.



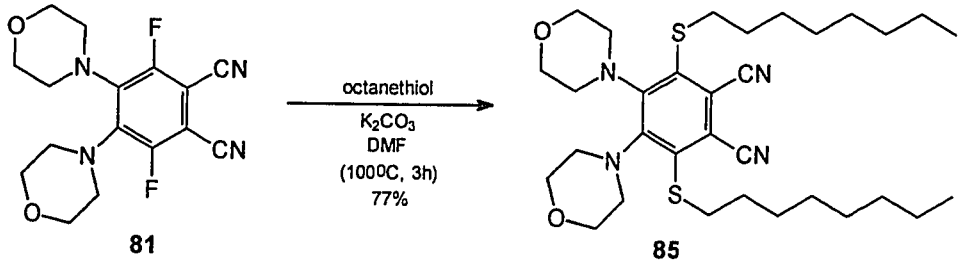
Scheme 26. Synthesis of 1,4,8,11,15,18,22,25-octafluoro-2,3,9,10,16,17,23,24-octamorpholinophthalocyanine nickel (II) (**82**)

Since compound **82** was only moderately soluble, the fluoro substituents on **81** were replaced with bulky or long chain groups which are known to enhance solubility. Thus, **81** reacted with an excess of neopentyl alcohol at 90°C in the presence of K_2CO_3 to give 4,5-dimorpholino-3,6-dineopentoxyphthalonitrile (**83**), Scheme 27. In comparison to tetrafluorophthalonitrile (**66**), sequential replacement of the fluoro substituents decreased the susceptibility of the phthalonitrile towards nucleophillic attack. For this reason, a large excess of neopentyl alcohol, long reaction times and high temperatures were required to drive the reaction to completion. Even under these conditions, a small amount of 3-fluoro-4,5-dimorpholino-6-neopentoxyphthalonitrile (**84**) remained. Separation of compounds **83** and **84** was possible by column chromatography.



Scheme 27. Synthesis of 4,5-dimorpholino-3,6-dineopentoxyphthalonitrile (**83**)

In contrast to the previous reaction, **81** reacted with two molar equivalents of 1-octanethiol in the presence of K_2CO_3 at 100°C for 3 h. This reaction proceeded quickly and cleanly to give **85** in a 77% yield (Scheme 28).



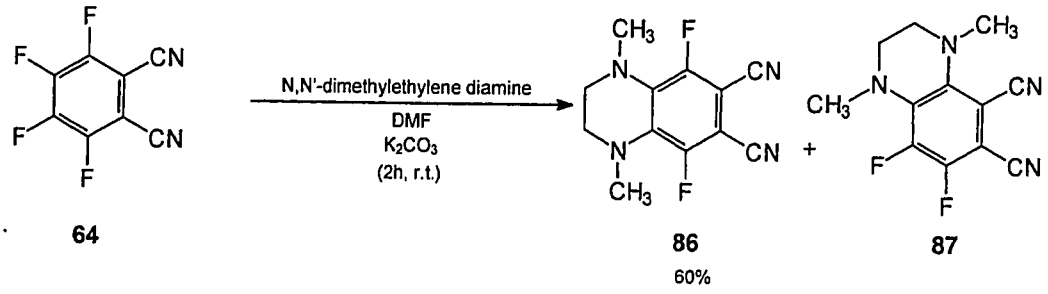
81 **85**

Scheme 28. Synthesis of 4,5-dimorpholino-3,6-dioctylthiophthalonitrile (**85**)

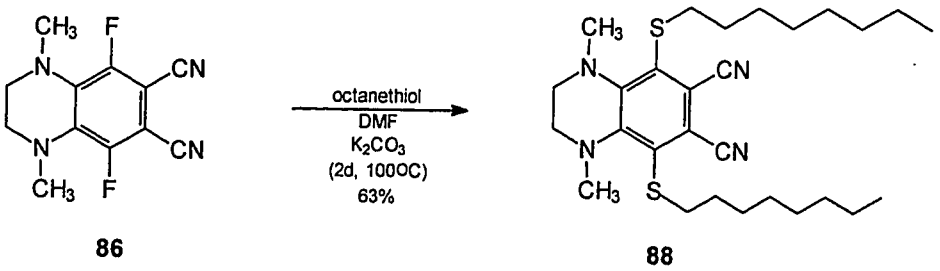
Attempts were made to self-condense the tetrasubstituted phthalonitriles (**83** and **85**) in refluxing DMAE in the presence of $NiCl_2$. These reactions were followed by UV-Visible spectroscopy and, even after 48 h, Q-band absorption peaks were not observed. Reaction of the tetrasubstituted phthalonitriles in a Li 1-octanolate/ 1-octanol solution at 100°C again did not produce any hexadecasubstituted Pcs as determined by UV-Visible spectroscopy.

It is suggested that steric hindrance between the bulky substituents of neighbouring phthalonitriles may be preventing phthalocyanine formation. Therefore, in an attempt to reduce some of the steric hindrance, the morpholino groups were replaced by a less bulky amine. In a reaction similar to the one outlined in Scheme 25, tetrafluorophthalonitrile **66** reacted with one molar

equivalent of N,N'-dimethylethylenediamine in DMF in the presence of K_2CO_3 at room temperature for 2 h (Scheme 29). Two isomeric products, **86** and **87**, were obtained and their separation was possible by crystallization. The symmetric isomer, **86**, subsequently reacted with 1-octanethiol in DMF in the presence of K_2CO_3 at 100°C for 48 h to afford **88** in a 63% yield (Scheme 30).



Scheme 29. Synthesis of 6,7-dicyano-5,8-difluoro-2,3-dihydro-1,4-dimethylquinoxaline (**86**)



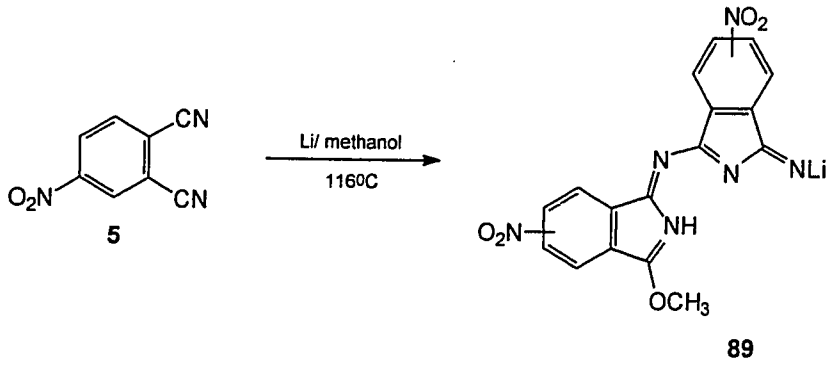
Scheme 30. Synthesis of 6,7-dicyano-2,3-dihydro-1,4-dimethyl-5,8-dioctylthioquinoxaline (**88**)

Condensation of the symmetric phthalonitrile **88** to the corresponding nickel phthalocyanine was attempted by heating under reflux in DMAE in the presence of $NiCl_2$ for 48 h. UV-Visible reaction probes revealed a minor Q-band absorption, however isolation of the phthalocyanine was not possible.

Cross-Condensation Reactions

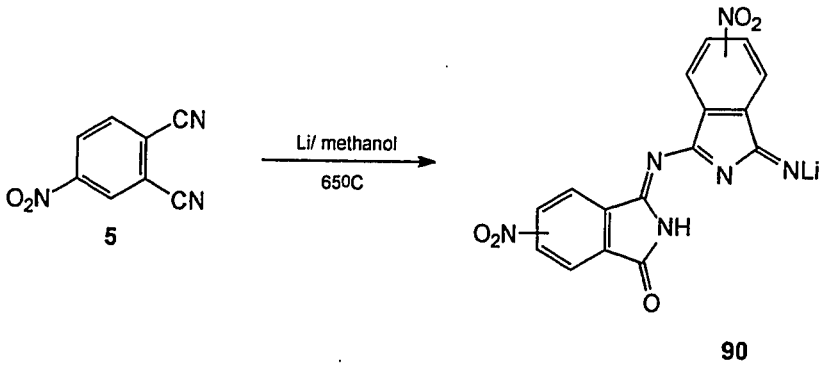
Synthesis of a monomeric intermediate

The synthesis of non-centrosymmetric phthalocyanines still remains a challenge. Generally a cross-condensation reaction involving two different phthalonitriles can yield a maximum of six phthalocyanines. Separation of these compounds, if at all possible, involves exhaustive chromatographic separation. In order to limit the number of phthalocyanine compounds formed, a synthetic route via phthalocyanine intermediates was envisioned. Our interest in synthesizing phthalocyanine intermediates was initiated by the work of Oliver and Smith [46]. Upon heating 4-nitrophthalonitrile in a lithium methoxide/ methanol solution to 116°C in a sealed tube, they obtained, based on mass spectral evidence, a dimeric intermediate (**89**), Scheme 31 [46].



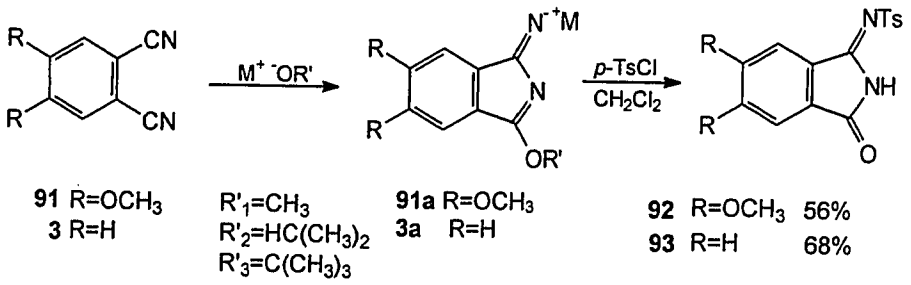
Scheme 31. Isolation of a dimeric intermediate

Repetition of this work by previous members of our group, using a lower temperature, i.e. that of refluxing methanol, gave a hydrolyzed product (**90**) (Scheme 32) [74]. Various other phthalonitriles were treated under similar conditions to determine whether they could be converted to their respective half-Pc intermediate. In all cases, it appeared that the desired intermediates formed, but their isolation was not possible since they were readily hydrolyzed and demetallated. Since isolation was not possible, attempts were made to protect the imine nitrogen using benzenesulfonyl chloride and trityl chloride. After several attempts under various conditions, protected intermediates could not be synthesized [74]. At this time, attention was turned towards an alternative strategy for synthesizing non-centrosymmetric phthalocyanines based on a monomeric intermediate.



Scheme 32. Attempted isolation of a dimeric intermediate

Although intermediates of the type **3a** are known to exist from the treatment of phthalonitrile (**3**) with sodium methoxide their purification may not be possible [75]. From work done on the dimeric intermediate, it had been determined that the problems of hydrolysis during purification would have to be addressed. To prevent hydrolysis of the exocyclic imine and to increase mobility during chromatography, *p*-toluenesulfonyl chloride was used as a protecting group. This method was applied toward the synthesis of protected intermediates (Scheme 33).



Scheme 33. Attempted isolation of monomeric intermediates

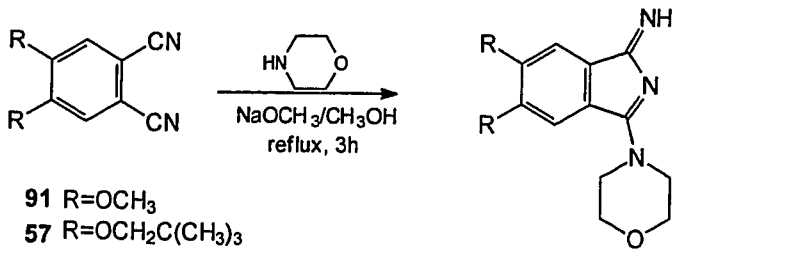
The first attempt in isolating a monomeric intermediate was performed by treating 4,5-dimethoxyphthalonitrile (**91**) with lithium methoxide in methanol (Scheme 33). This crude product was then protected by treatment with *p*-toluenesulfonyl chloride in methylene chloride. Purification was accomplished

using preparative silica gel TLC plates only to afford a hydrolyzed product, compound **92**, in a 56% yield. Hydrolysis may have been caused by the silica gel, due to its acidic nature. Separation therefore was attempted by gel permeation chromatography using SX-2 Biobeads® but, unfortunately, without success.

It was hoped that repetition of the above reaction using bulkier alcohols would result in the formation of a product that is less susceptible to hydrolysis. For this reason, **91** and **3** were treated with isopropyl and tert-butyl alcohol. Although different nucleophiles were used to initiate the cyclization process, identical products were always isolated. Hydrolyzed products **92** and **93** were obtained from **91** and **3,** respectively (Scheme 33).

In a variation of the previous reactions, it was decided to treat the phthalonitriles with an amine in place of the alcohols as the nucleophile. This substitution should facilitate isolation of the intermediate, since amines have been successfully added to phthalonitriles to yield *N*-substituted derivatives of diiminoisoindoline [76]. In addition to this, diiminoisindoline has also been treated with various amines to yield *N*-substituted adducts [77-82]. Reaction of the dimethoxyphthalonitrile **91** with morpholine in a $NaOCH_3$ / methanol solution proceeded at reflux for 3 h to afford, upon cooling, crystals of compound **94** in an 81% yield (Scheme 34). Similarly, repetition of this reaction using 4,5-

dineopentoxyphthalonitrile **57** in place of **91** afforded compound **95** (Scheme 34) in a 73% yield.



91 R=OCH_3
57 R=$OCH_2C(CH_3)_3$

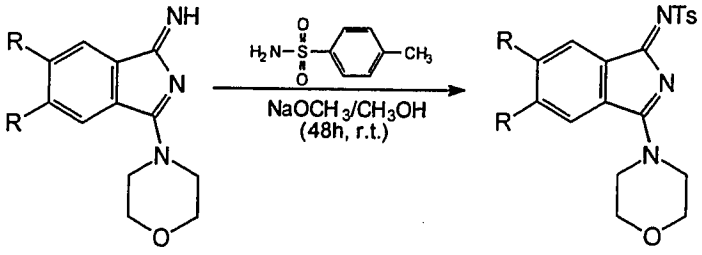
94 R=OCH_3 81%
95 R=$OCH_2C(CH_3)_3$ 73%

Scheme 34. Synthesis of monomeric intermediates **94** and **95**

Under the reaction conditions used to synthesize the above mentioned intermediates, phthalocyanine formation did not occur. This is not surprising since Pc formation occurs very slowly in the lower molecular-weight alcohols [27, 83]. It should be possible however, to convert these compounds to their corresponding octaalkoxyphthalocyanines by continuing the cyclization process. Self-condensation of compound **91** in DMF at 80°C did lead to the formation of metal-free 2,3,9,10,16,17,23,24-octamethoxyphthalocyanine in a 15% yield, but this yield was not optimized.

Since **94** and **95** are capable of undergoing self-condensation, they cannot be used in a cross-condensation reaction until the exocyclic imine is protected.

In a variation of the reactions shown in Scheme 33, the intermediates **94** and **95** reacted with *p*-toluenesulfonamide in place of *p*-toluenesulfonyl chloride as the protecting group. In the reactions with *p*-toluenesulfonyl chloride, HCl was obtained as a by-product and this may have been causing hydrolysis of the intermediate. Thus, treatment of compound **94** with *p*-toluenesulfonamide in methanol at room temperature afforded the tosylated product, compound **96** (Scheme 35). This compound was obtained as a yellow colored solid in a 75% yield. Similarly, repetition of this reaction using **95** gave compound **97** as a yellow colored solid in a 78% yield (Scheme 35).



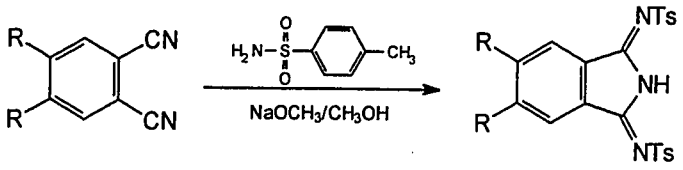
94 R=OCH_3
95 R=$OCH_2C(CH_3)_3$

96 R=OCH_3 75%
97 R=$OCH_2C(CH_3)_3$ 78%

Scheme 35. Synthesis of protected monomeric intermediates **96** and **97**

An alternative class of intermediates resembling ditosylated diiminoisoindolines was also synthesized. It was speculated that the presence of two electron-withdrawing tosyl groups would enhance the intermediate's

susceptibility towards nucleophilic attack. Synthesis of the protected intermediate was performed by treating 4,5-dineopentoxyphthalonitrile (**57**) with two molar equivalents of *p*-toluenesulfonamide, to yield compound **98** (Scheme 36). Similarly, reaction of the dimethoxyphthalonitrile **91** and phthalonitrile (**3**) with two molar equivalents of *p*-toluenesulfonamide gave the doubly protected intermediates **99** and **100** (Scheme 36). Surprisingly, a monotosylated product could not be obtained by treating phthalonitrile with one molar equivalent of *p*-toluenesulfonamide. Even under these conditions, the doubly protected intermediate still formed. Compounds **98-100** were obtained in 35% to 60% yield and were fully characterized by ^{1}H-NMR, ^{13}C-NMR, EI-MS, IR and elemental analysis.



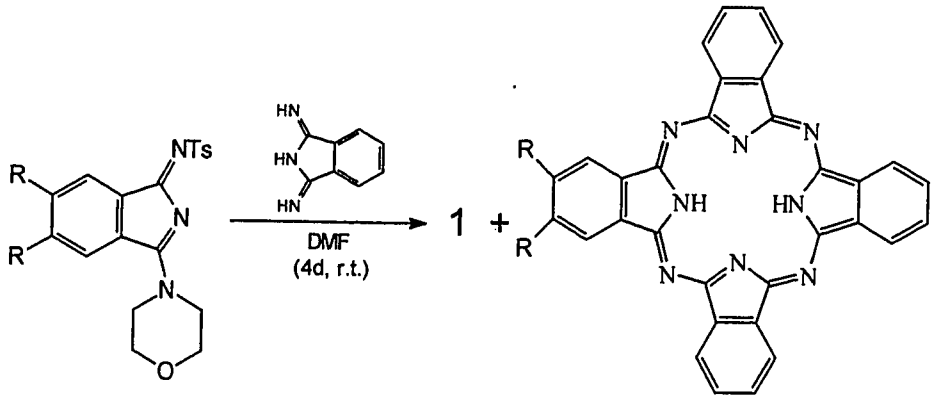
57 R=$OCH_2C(CH_3)_3$
91 R=OCH_3
3 R=H

98 R=$OCH_2C(CH_3)_3$ 35%
99 R=OCH_3 15%
100 R=H 60%

Scheme 36. Synthesis of ditosylated intermediates **98-100**

In an attempt to synthesize a mixed phthalocyanine, a cross-condensation reaction was carried out using a one-to-one mole ratio of compound **97** and

diiminoisoindoline (**4**) in DMF (Scheme 37). Under these reaction conditions, a maximum of three different Pcs can be formed: 2,3-dineopentoxy Pc, 1,2,16,17-tetraneopentoxy Pc (ABAB Pc) and unsubstituted Pc. To minimize the formation of unsubstituted Pc by the self-condensation of diiminoisoindoline, the reaction was performed at room temperature. Under these reaction conditions, unsubstituted Pc formed along with what is believed to be 2,3-dineopentoxy phthalocyanine (**101**). A FABMS of this compound showed a mass cluster at 686 mass units which corresponds to the molecular weight of **101**. Since compound **101** was formed in a crude yield of approximately 3%, this reaction was not pursued any further.



97 R=$OCH_2C(CH_3)_3$

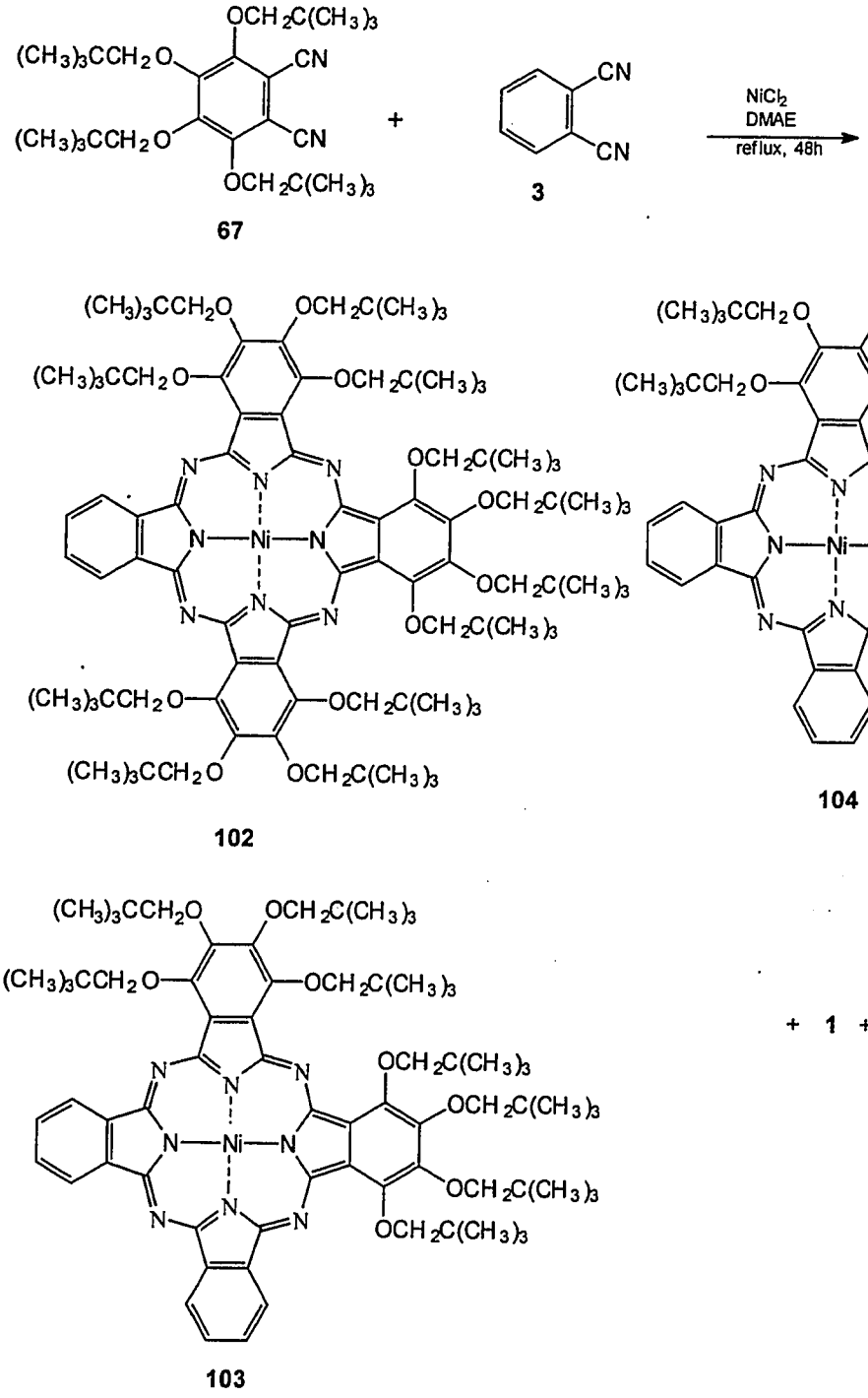
101 R=$OCH_2C(CH_3)_3$

Scheme 37. Synthesis of non-centrosymmetric phthalocyanine **101**

It was felt that compounds **98-100** would be highly susceptible to nucleophillic attack by diiminoisoindoline since these compounds contain two electron-withdrawing tosyl groups. Unfortunately, a cross-condensation reaction using a one-to-one mole ratio of compound **98** and diiminoisoindoline (**4**) in DMF at room temperature only produced unsubstituted Pc. It is possible that the tosyl groups were too bulky to permit attack by diiminoisoindoline.

Cross-condensation Reactions Involving Tetrasubstituted Phthalonitriles

To determine if the tetrasubstituted phthalonitriles could be used in the synthesis of non-centrosymmetric phthalocyanines, cross-condensation reactions between them and phthalonitrile (**3**) were carried out. As previously mentioned, cross-condensation reactions involving two different phthalonitriles can yield a maximum of six different phthalocyanines. Some of these products can be avoided by using a large excess of one of the phthalonitriles. If a large excess of phthalonitrile (**3**) is used, then mostly unsubstituted phthalocyanine and 1,2,3,4-substituted phthalocyanines should be obtained. Surprisingly, however, when 3,4,5,6-tetraneopentoxyphthalonitrile (**67**) reacted with **3** in a 1 : 10 mole ratio in the presence of $NiCl_2$, five different phthalocyanines were obtained (Scheme 38). Purification of these compounds involved Soxhlet-extracting the crude reaction mixture with benzene to remove soluble Pcs from the unsubstituted Pc Ni (**1**), followed by flash silica gel column chromatography of the soluble Pc fractions.



Scheme 38. Synthesis of non-centrosymmetric Pcs **102-104**

Since a large excess of unsubstituted phthalonitrile (**3**) was used, in comparison to **67**, formation of **68** and 1,2,3,4,8,9,10,11,15,16,17,18-dodecaneopentoxyphthalocyanine nickel (II) (**102**) did not seem likely. Only trace amounts of compound **68** were obtained, but **102** was obtained in a 3% yield. Identification of the latter compound was based on MALDI-MS, ^{1}H- and ^{13}C-NMR spectroscopy. Analysis of the MALDI-MS showed an ion signal at m/z 1603.2 corresponding to the molecular weight of the parent ion. As expected, the ^{1}H-NMR spectrum (Figure 9) revealed two non-equivalent aromatic protons and six non-equivalent neopentoxy groups. Also, the ^{13}C-NMR spectrum (Figure 9) confirmed the presence of the six non-equivalent neopentoxy groups. Formation of **102** may have occurred due to the difference in reactivity of the two phthalonitriles. The tetrasubstituted phthalonitrile (**67**), probably due to its steric bulk, reacted very slowly in comparison to **3**. Therefore it is possible that during the course of the reaction, **3** was readily converted to phthalocyanine while the tetrasubstituted phthalonitrile remained unreacted. As the reaction proceeded, the ratio of **3** to **67** shifted to an excess of **67**. Under these conditions formation of **102** is possible.

Another product whose formation did not seem likely was the AABB substituted 1,2,3,4,8,9,10,11-octaneopentoxyphthalocyanine nickel (**103**). It was felt that the steric bulk of the neopentoxy groups would favour the formation of its

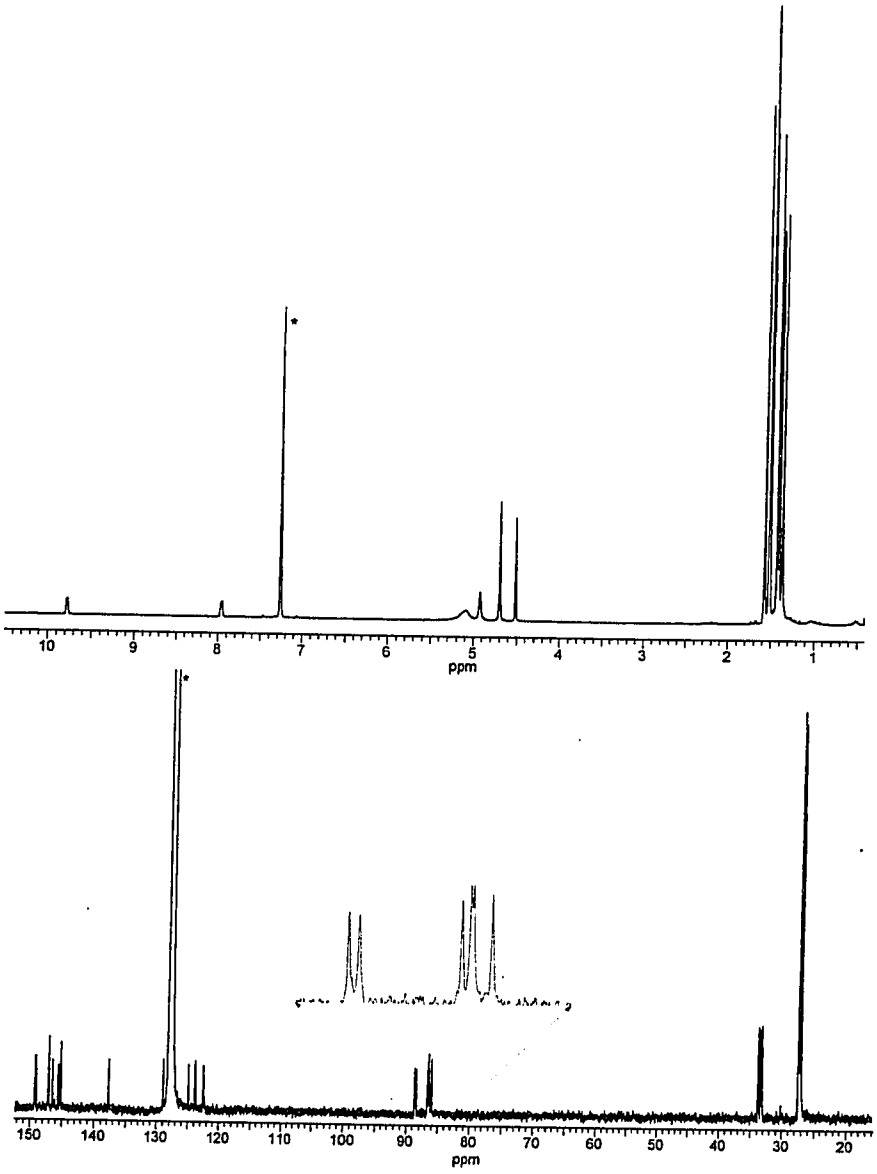


Figure 9. The ^{1}H- and ^{13}C-NMR spectra of **102** in benzene-d_6 (solvent peaks have been marked with an asterisk (*))

isomer, the ABAB substituted phthalocyanine. Surprisingly, **103** was obtained in a 3% yield and the ABAB substituted phthalocyanine was not observed. Generally, in cross condensation reactions in which one of the phthalonitriles is substituted with bulky substituents, formation of the ABAB substituted phthalocyanine is favoured over formation of the AABB substituted phthalocyanine. However, it has been shown that when long chain substituents are preset in the 1,4,8,11,15,18,22,25-postiions the relative yields of ABAB and AABB substituted phthalocyanines are equal [84]. Formation of AABB substituted phthalocyanine may be accounted for by non-polar interactions occurring between the long chain alkoxy groups since these reactions are taking place in a polar solvent. In addition to this, dimeric type intermediates have been isolated in cases where nickel was used as a metal template during phthalocyanine formation. The presence of these types of intermediates would again favour formation of the AABB substituted phthalocyanine [63].

Analysis of the MALDI-MS showed an ion signal at m/z 1258.5 corresponding to the molecular weight of the parent ion. This molecular weight may be assigned to either the AABB or ABAB substituted phthalocyanine and in order to differentiate between them, ^{1}H- and ^{13}C-NMR spectroscopy were used. AABB substituted phthalocyanines belong to the C_{2v} point group, whereas ABAB

substituted phthalocyanines belong to the D_{2h} point group. This difference results in unique splitting patterns which can be used to determine which isomer is present. The aromatic region of the ^{1}H-NMR spectrum (Figure 10) consisted of two doublets and a multiplet corresponding to the 4 non-equivalent aromatic protons. In other regions of the spectrum, signals corresponding to four non-equivalent neopentoxy groups were observed. If the more highly symmetric ABAB substituted phthalocyanine had formed, then only two non-equivalent aromatic protons signals should have been present, along with signals corresponding to only two non-equivalent neopentoxy groups.

Also, ^{13}C-NMR spectroscopy was used to confirm the presence of the AABB substituted phthalocyanine isomer. As expected for compound **103**, the ^{13}C-NMR spectrum (Figure 10) displayed signals corresponding to four non-equivalent neopentoxy groups and sixteen signals corresponding to the phthalocyanine macrocycle. Again, the ABAB phthalocyanine would display fewer signals for the neopentoxy groups and the phthalocyanine macrocycle.

Furthermore, **103** displayed a single Q-band absorption, which is in accordance with what is generally observed for AABB substituted phthalocyanines, which are of C_{2v} symmetry [84]. In the case of ABAB substituted phthalocyanines, which are of D_{2h} symmetry, a split Q-band absorption is generally observed [43, 44].

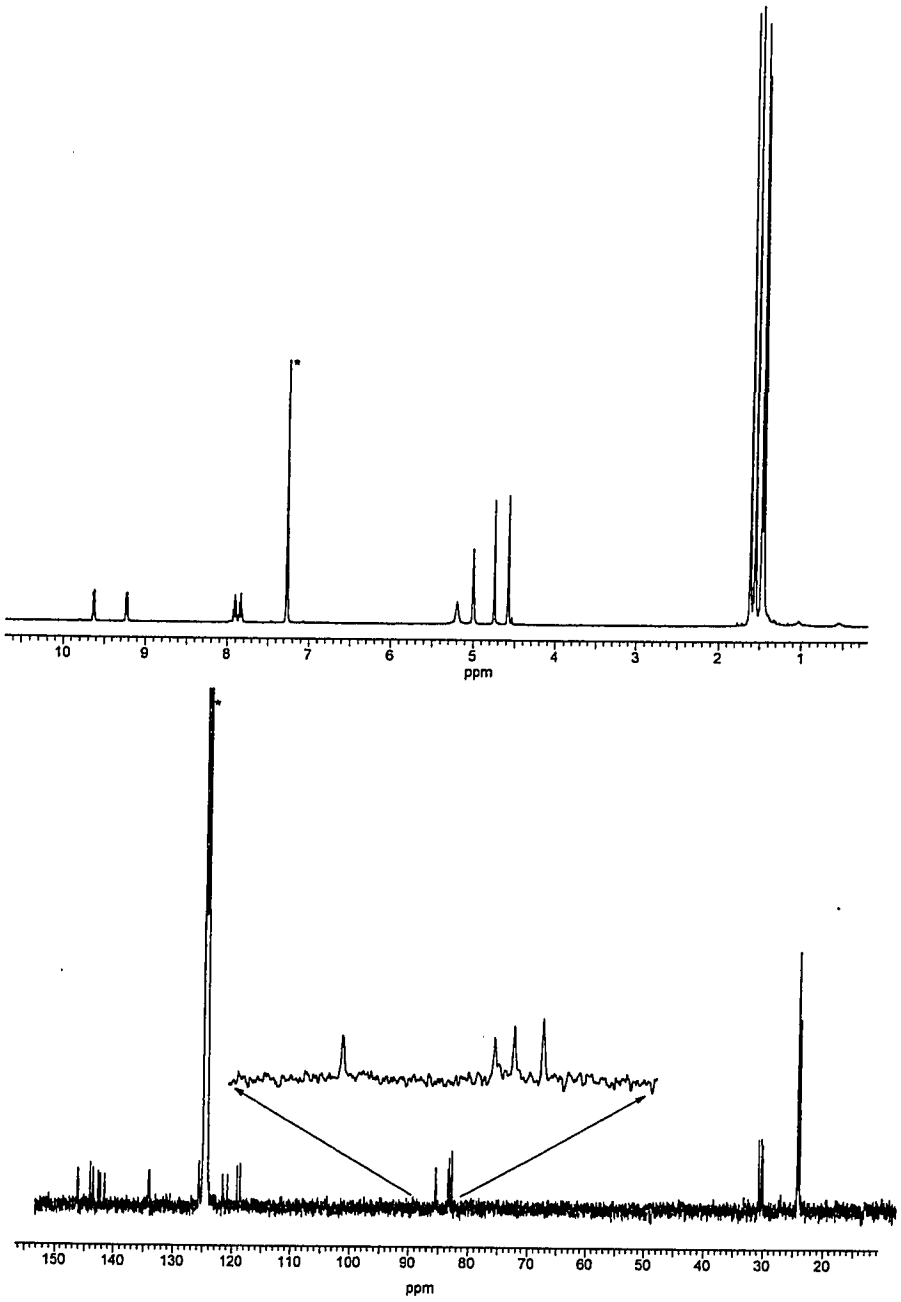
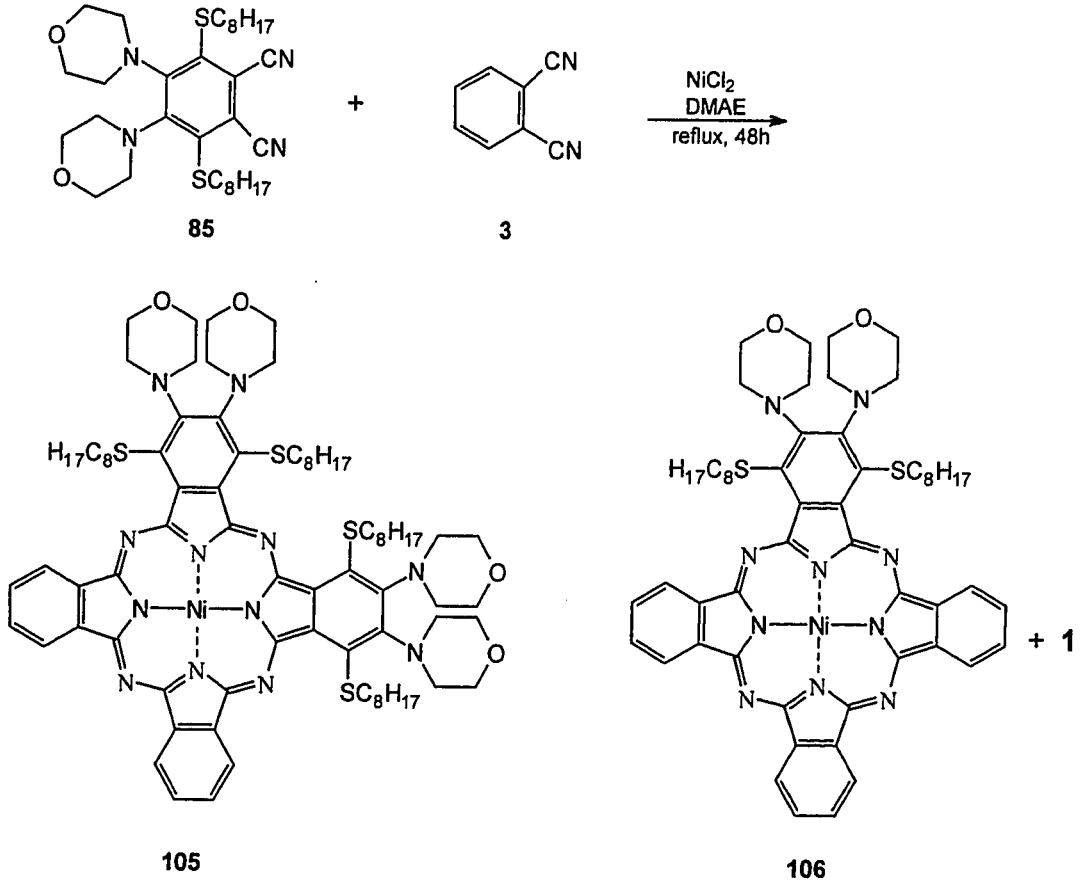


Figure 10. The ^{1}H- and ^{13}C-NMR spectra of **103** in benzene-d_6 (solvent peaks have been marked with an asterisk (*))

Also formed in this reaction was the 1,2,3,4-tetraneopentoxy-phthalocyanine nickel (II) (**104**) in a 2% yield. MALDI-MS and ^{1}H-NMR spectroscopy were used to determine the structure of this compound. Analysis of the MALDI-MS showed an ion signal at m/z 1186.7, which corresponds to the molecular weight of the parent ion. The aromatic region of the ^{1}H-NMR spectrum consisted of signals corresponding to six protons. Two singlets, with a total integration of four protons, were observed for the OCH_2 protons and two singlets, with a total integration of eighteen, were observed for the $C(CH_3)_3$ protons.

Since compounds **83** and **85** did not self-condense to form phthalocyanine, it was felt that cross-condensation reactions using these phthalonitriles would give a limited number of products. Compound **85** reacted with unsubstituted phthalonitrile in a 1:10 mole ratio in the presence of $NiCl_2$ for 48 h in refluxing DMAE to yield two substituted Pcs (Scheme 39). Purification involved removing the soluble substituted Pcs from the unsubstituted PcNi by Soxhlet extraction using benzene. The benzene-soluble phthalocyanines were chromatographed on a flash silica gel column using 50% ethyl acetate/ 50% hexane as eluent. All of the green/blue fractions were further chromatographed on an SX-3 Biobeads® column using toluene as eluent. Two distinct bands separated and these were re-chromatographed on a flash silica gel column.

After exhaustive purification, the AABB substituted 2,3,9,10-tetramorpholino-1,4,8,11-tetraoctylthiophthalocyanine nickel (II) (**105**) and 2,3-dimorpholino-1,4-dioctylthiophthalocyanine nickel (II) (**106**) were obtained in 2 % and 4 % yield, respectively.



Scheme 39. Synthesis of non-centrosymmetric Pcs **105** and **106**

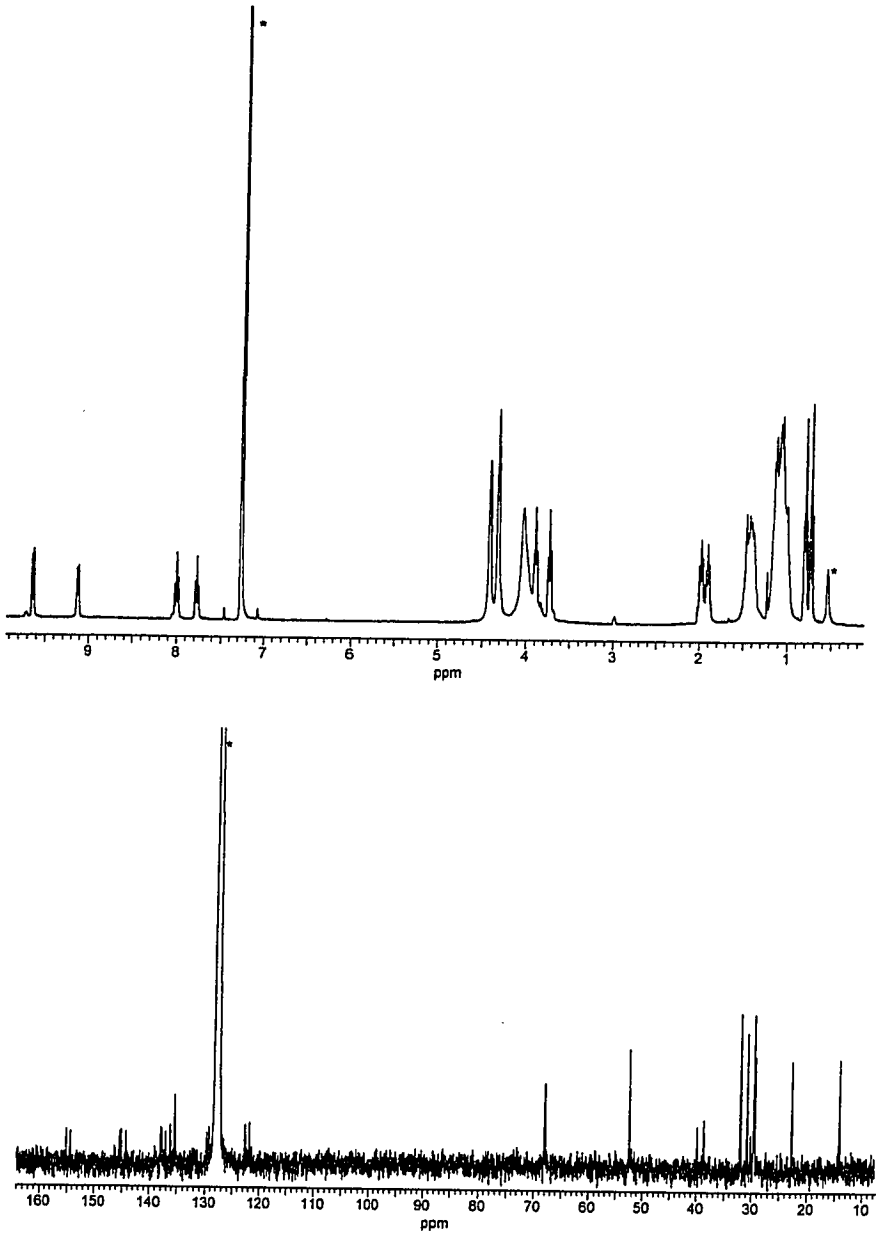


Figure 11. The ^{1}H- and ^{13}C-NMR spectra of **105** in benzene-d_6 (solvent peaks have been marked with an asterisk (*))

Characterization of **105** was based on MALDI-MS and ^{1}H-NMR analysis. Analysis of the MALDI-MS showed an ion signal at m/z 1487.9, which corresponded to the molecular weight of the parent ion. The ^{1}H-NMR spectrum (Figure 11) revealed four non-equivalent aromatic protons and two non-equivalent morpholino and octylthio groups. If the more highly symmetric ABAB substituted phthalocyanine had formed, then the ^{1}H-NMR would display signals corresponding to only two non-equivalent aromatic protons and one non-equivalent morpholino and octylthio substituents each. In addition to this, the ^{13}C-NMR (Figure 11) revealed 16 signals corresponding to the phthalocyanine macrocyclic.

The second product of this cross-condensation reaction was compound **106**. Identification of this compound was based on MALDI-MS and ^{1}H-NMR spectroscopy. Analysis of the MALDI-MS showed an ion signal at m/z 1029.4, which corresponds to the molecular weight of the parent ion. In the aromatic region of the ^{1}H-NMR spectrum (Figure 12), six signals of equal intensity were observed. Analysis of other regions of the spectrum revealed the presence of only one unique morpholino and one octylthio substituents. Elemental analysis of compounds **102-106** did not give the percent composition of carbon, hydrogen and nitrogen within the acceptable range. This is not uncommon since phthalocyanines are known to be resistant to combustion [85].

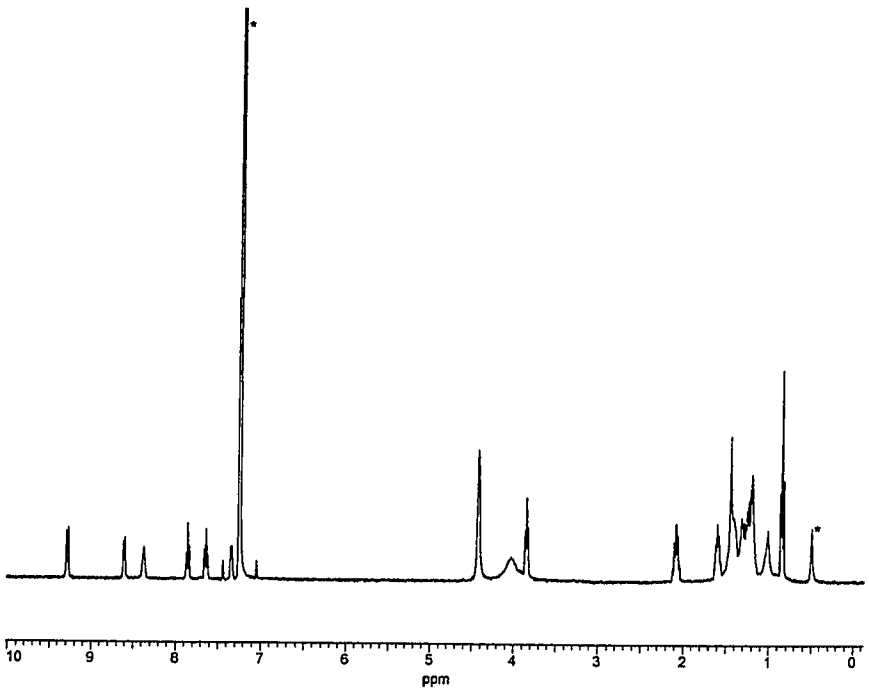
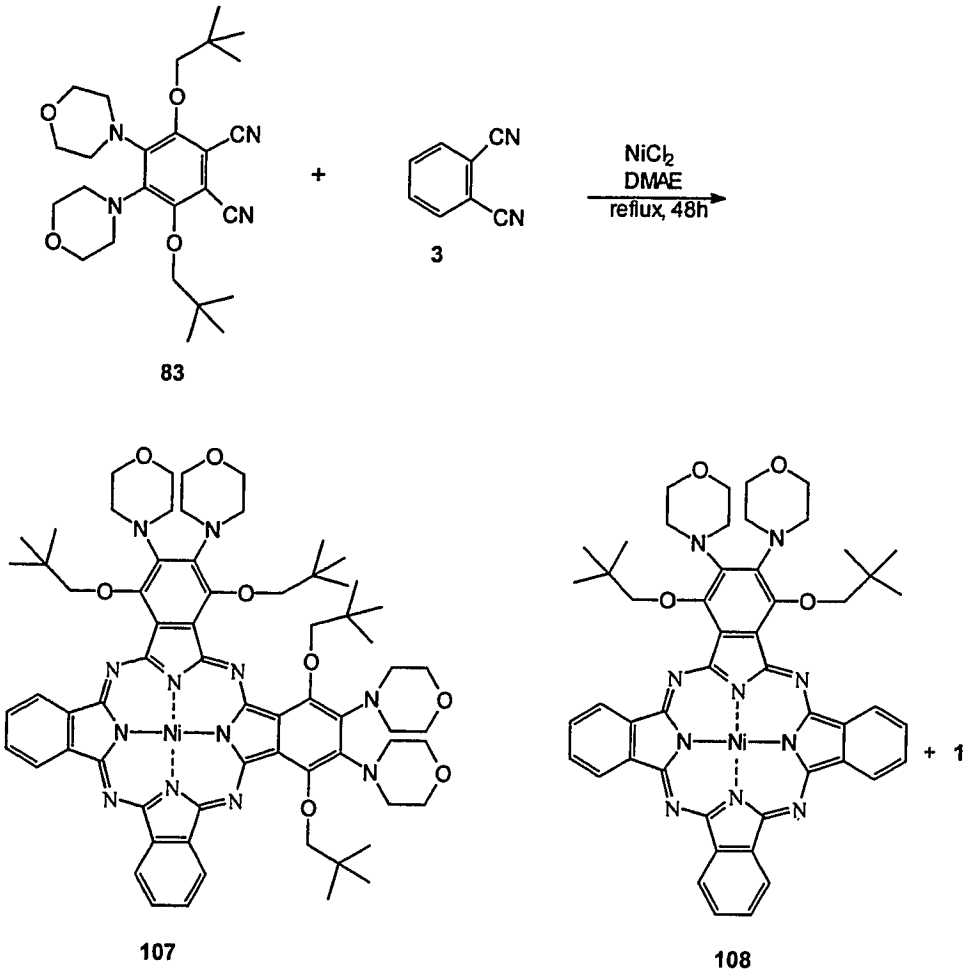


Figure 12. The ^{1}H-NMR spectrum of **106** in benzene-d_6 (solvent peaks have been marked with an asterisk (*)

A cross-condensation reaction between compound **83** and unsubstituted phthalonitrile also gave only two types of substituted phthalocyanines, Scheme 40. MALDI mass spectral analysis showed the expected molecular ion at m/z 1254.6, corresponding to compound **107**, and a molecular ion at m/z = 912.1, corresponding to compound **108**. Unfortunately, even after extensive purification by gel permeation and silica gel chromatography, pure samples, as determined by ^{1}H-NMR spectroscopy, could not be obtained.



Scheme 40. Synthesis of non-centrosymmetric Pcs **107** and **108**

In an attempt to synthesize non-centrosymmetric phthalocyanines containing electron-wtihdrawing and electron-donating substituents, which would enhance the Pc's dipole moment [86, 87], **85** was treated with a large excess of 4-nitrophthalonitrile (**5**). Unfortunately, purification of the reaction mixture was not possible due to the low solubility of the phthalocyanine in many of the common organic solvents.

VARIABLE TEMPERATURE ^{1}H-NMR STUDIES

Examination of the ^{1}H-NMR spectra of the two octaneopentoxy phthalocyanines **65** and **62** at room temperature in benzene-d_6 revealed the expected three singlets for each compound. Peaks were observed at 7.40, 4.39 and 1.17 ppm for **65** representing the aromatic, alkoxy, and *tert*-butyl protons respectively, and similarly, absorptions at 8.93, 3.88 and 1.26 ppm were present for **62**. In the ^{1}H-NMR spectrum at room temperature (298 K) of the hexadecaneopentoxyphthalocyanine **68**, two different alkoxy and *tert*-butyl absorptions representing the two different positions of the neopentoxy groups were expected. However, two peaks at 1.39 (9 H) and 1.22 ppm (9 H) for the two different *tert*-butyl signals were present but only a single peak at 4.55 ppm (2 H) corresponding to one of the OCH_2 groups was observed. Though one alkoxy group was missing, a faint bulge in the baseline at ~ 4–5 ppm suggested that restricted rotation of the neopentoxy groups was the likely reason for its absence. Thus, **65**, **68**, and **62** were all subjected to temperature-dependent NMR studies to examine this phenomenon, well known in other related systems including porphyrins [88], neopentylbenzenes [89-91], neopentylnaphthalenes [92], but to the best of our knowledge not phthalocyanines. Table 2 summarizes the relevant thermokinetic parameters obtained from standard lineshape analyses for the three phthalocyanines reported in this work.

Figure 13 shows the spectral changes observed in the OCH_2 region of Pc **68** from 205 K to 355 K in toluene-d_8. The ^{1}H-NMR spectrum of **68** at room temperature exhibited two different *tert*-butyl groups as expected, but only a single OCH_2 peak. As the temperature of the sample was increased during the NMR experiment, a new singlet appeared and sharpened. It seemed as if free rotation of all neopentoxy groups was occurring at 355 K. In attempts to freeze out rotations of **68**, its NMR spectrum was analyzed at lower temperatures. As the temperature was decreased below 275 K, the OCH_2 peak began to broaden. Around 260 K, this OCH_2 peak began splitting into two separate peaks, and two new OCH_2 signals began to appear on either side of it. At 235 K, the neopentoxy OCH_2 groups, presumably in the 2,3,9,10,16,17,23,24- positions, showed splitting typical of an AB quartet centered at 4.61 ppm. The 1,4,8,11,15,18,22,25-neopentoxy-CH_2O groups showed a widely separated AX quartet with doublets appearing at 6.05 and 3.88 ppm. These results suggest that all the neopentoxy groups are relatively fixed on the NMR time scale at 235 K and that **68** probably occurs as a single atropisomer with the 16 neopentoxy groups arranged in an alternating up (u), down (d), u,d,u,d,u,d,u,d,u,d,u,d,u,d configuration, as shown in Figure 14.

Lineshape analyses of both OCH_2 signals according to a two-site, equal-population coupled exchange model [93-95] corresponding to two pairs of

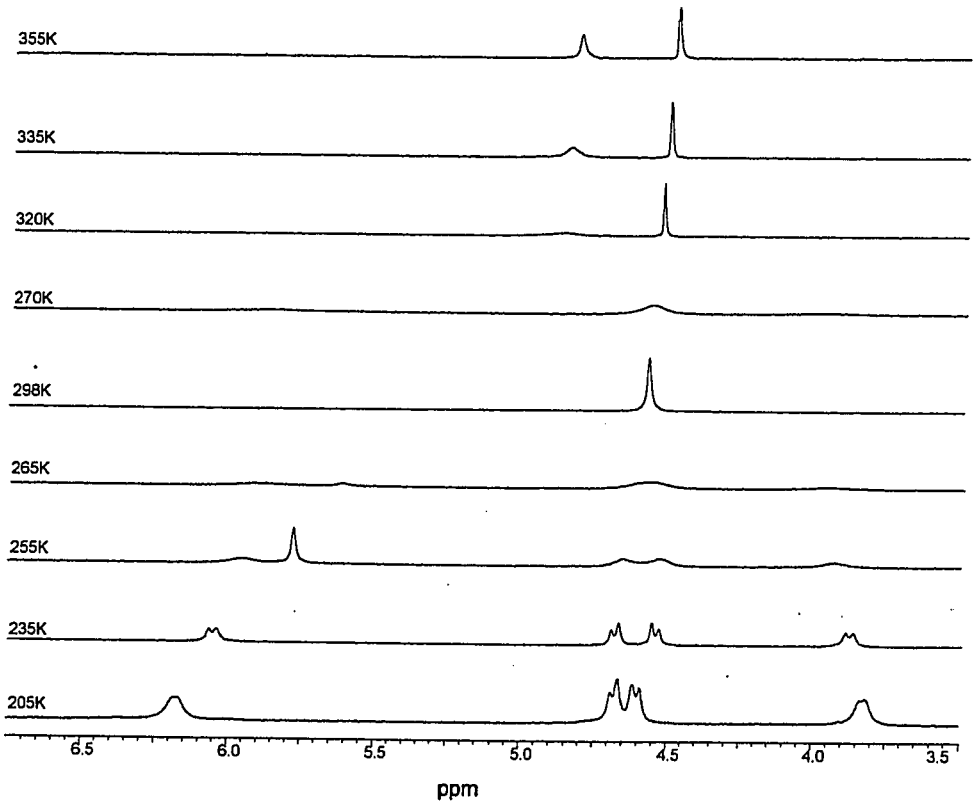
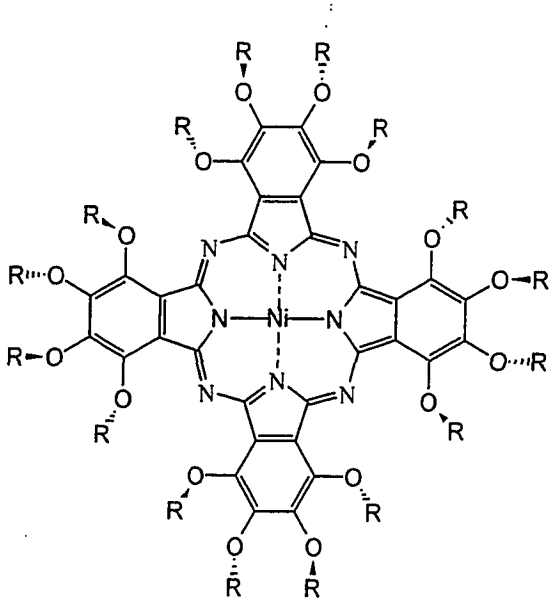


Figure 13. ^{1}H-NMR spectrum of **68** in toluene-d_8 showing spectral changes in the OCH_2 region from 355 K to 205 K



68 R = $OCH_2C(CH_3)_3$

Figure 14. Suggested conformation of **68**

diastereotopic protons confirmed the steric demands imposed by the neopentoxy groups. Nearly identical results were obtained for each OCH_2 group: an enthalpy of activation of about 10 kcal mol^{-1} and a negative valued entropy of activation of about -10 cal K^{-1} mol^{-1} that contributed to a free energy of activation of about 13 kcal mol^{-1}. These findings give support for correlated motions in the neopentoxy groups.

Figure 15 shows the spectral changes observed in the OCH_2 region of Pc **62** from 225 K to 300 K in toluene-d_8. At room temperature, the ^{1}H-NMR

spectrum showed the expected three singlets at 8.95, 3.85 and 1.28 ppm for the aromatic, OCH_2 and *tert*-butyl groups respectively (Figure 15). At 260 K, significant broadening occurred in all the peaks to the point where they almost disappeared into the baseline. At 235 K, the aromatic region of the spectrum consisted of two distinct peaks of equal intensity at 9.31 and 8.62 ppm. In other regions of the spectrum, three peaks (1H, 2H, 1H) were present in the OCH_2 region, whereas two peaks of equal intensity were present for the *tert*-butyl groups. Further lowering of the temperature (225 K) gave two peaks of unequal intensity for both the aromatic protons and *tert*-butyl groups. In the OCH_2 region, three peaks of unequal intensity were observed. These data suggest that **62** exists as a mixture of two populations of atropisomers.

Lineshape analyses according to an unequal-population, two-site exchange model [95] resulted in a population distribution of $p_A = 0.56$ and $p_B = 0.44$ and estimates of free energy barriers of about 12 kcal mol^{-1} for the aromatic, OCH_2 and *tert*-butyl regions of the spectrum. These barriers were consistent with those found for **68**, as would be expected for interaction between neopentoxy groups ortho to one another.

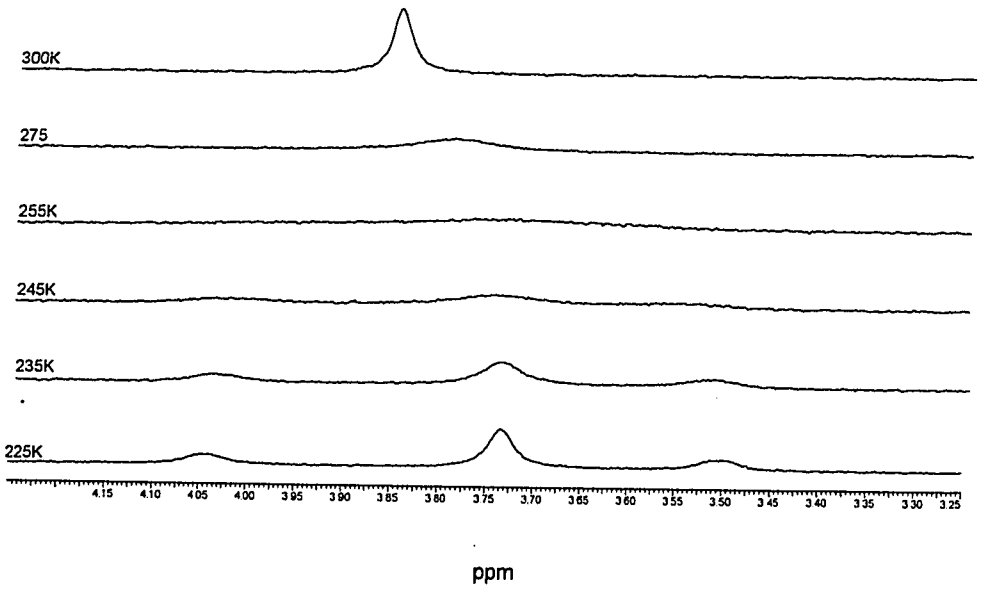


Figure 15a. ^{1}H-NMR spectrum of **62** in toluene-d_8 showing spectral changes in the OCH_2 region from 300 K to 225 K

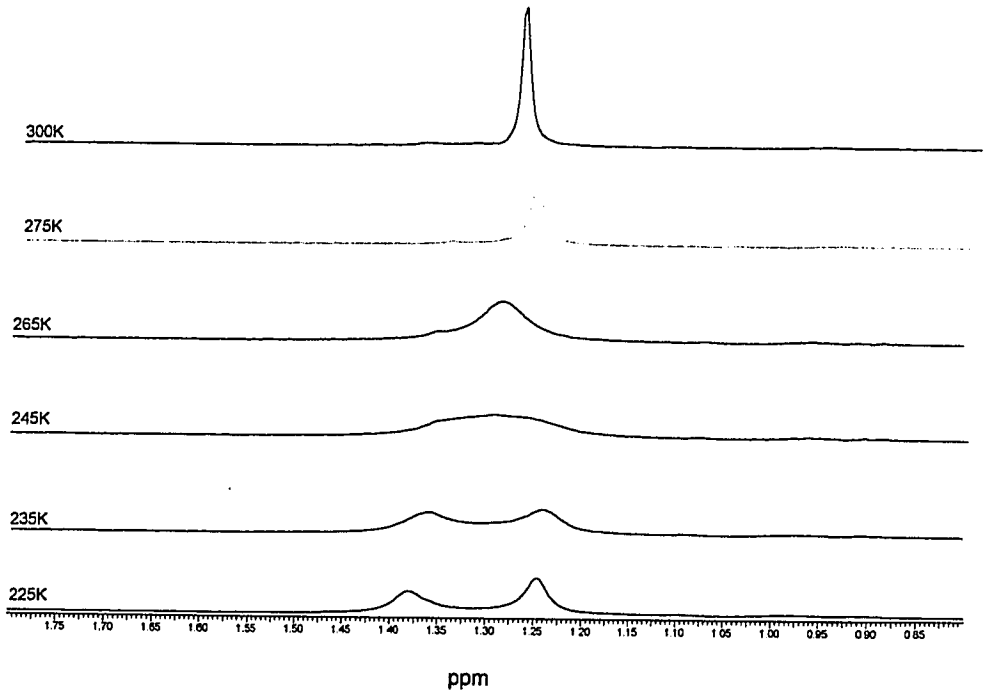


Figure 15b. ^{1}H-NMR spectrum of **62** in toluene-d_8 showing spectral changes in the t-butyl region from 300 K to 225 K

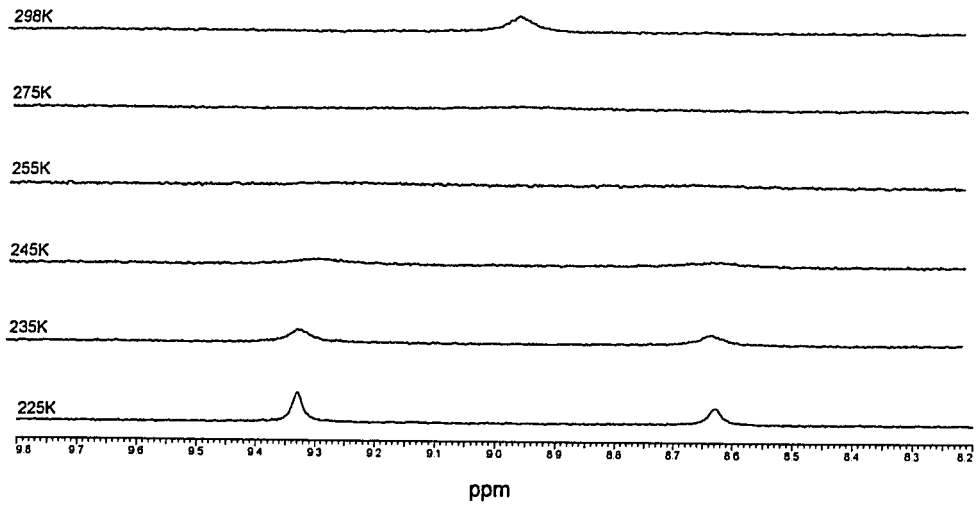


Figure 15c. ^{1}H-NMR spectrum of **62** in toluene-d_8 showing spectral changes in the aromatic region from 300 K to 225 K

Figure 16 shows the spectral changes observed in the OCH_2 region of Pc **65** from 200 K to 300 K in toluene-d_8 solvent. At room temperature, the ^{1}H-NMR of **65** showed the expected three singlets at 7.37, 4.38 and 1.20 ppm for the aromatic, OCH_2 and *tert*-butyl groups respectively. The sharp singlet for the OCH_2 remained sharp until 225 K when significant broadening occurred. By 205 K, the singlet split into two separate peaks but, at this temperature, the two protons still did not split each other as would be expected for diastereotopic protons. The series of spectra in this region were subjected to lineshape analyses according to an equal-population, uncoupled, two-site exchange model [69-71]. The resulting thermokinetic parameters were as follows: $\Delta H^{\ddagger}$ = 15.6 ± 0.7 kcal mol^{-1}, $\Delta S^{\ddagger}$ = 25.6 ± 3.5 cal K^{-1} mol^{-1} and $\Delta G_{298}^{\ddagger}$ = 8.0 ± 0.3 kcal mol^{-1}.

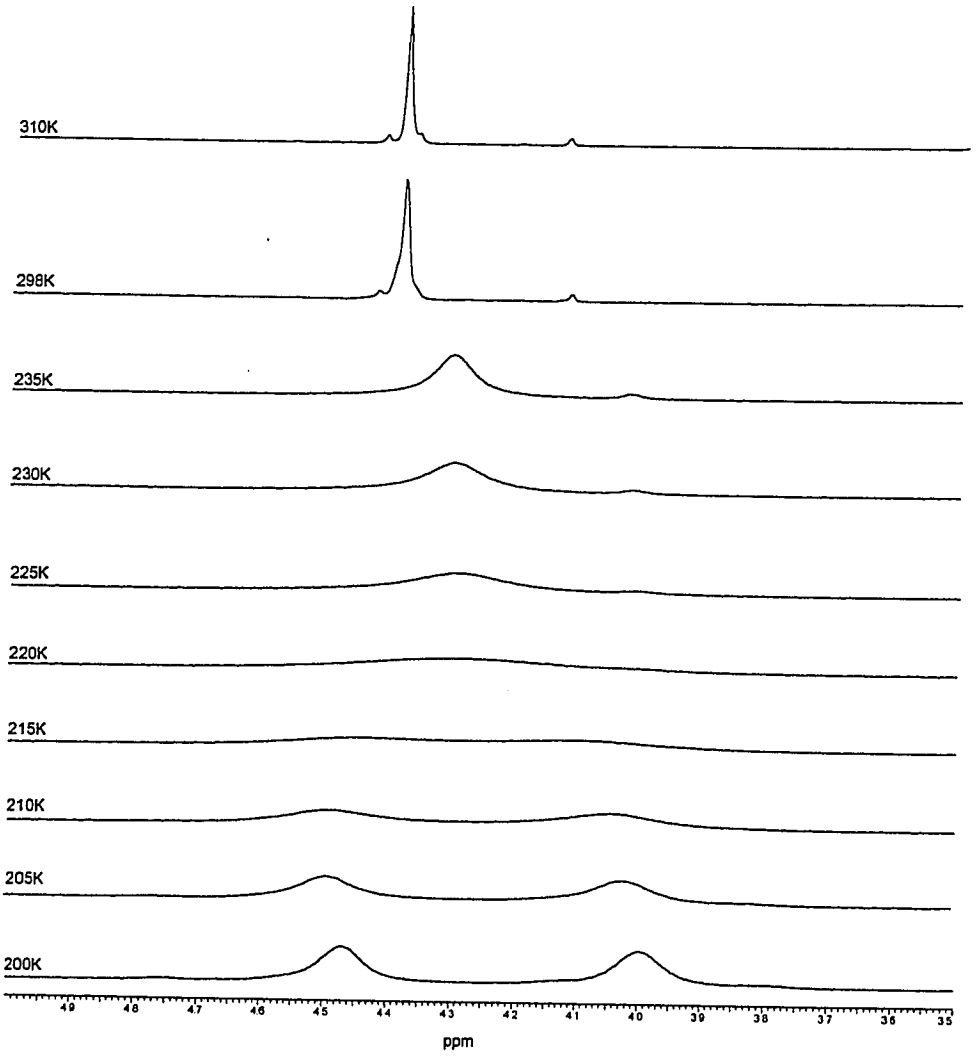


Figure 16. ^{1}H-NMR spectrum of **65** in toluene-d_8 showing spectral changes in the OCH_2 region from 310 K to 200 K

Estimates of the entropy are approximately 26, -10 and 7cal K^{-1} mol^{-1} for compounds **65**, **68** and **62**, respectively. These values are consistent with **65** having the highest degree of freedom for motion of the neopentoxy groups and **68** having the least freedom of motion. A comparison of the enthalpy values shows that compound **65** experiences the least deformation in the transition state. Also, the free energy of activation, as expected, was found to be the lowest for **65** and largest for **68**. Although this phenomenon of restricted rotation has never been observed in phthalocyanines, it had been observed in neopentylbenzenes. In the case of highly substituted compounds such as 3,4,5,6-tetramethyl-1,2-dineopentylbenzene, a free energy of rotation of 11.5 Kcal/mol was calculated [96]. Similarly, the congested 1,3-dimethyl-2,4,6-trineopentylbenzene had a free energy of rotation of 15.0 Kcal/mol [90]. These values are comparable to the free energy of rotation calculated for the congested phthalocyanines **68** and **62**.

Table 2. Summary of thermokinetic parameters obtained from lineshape analyses performed on various regions of ^{1}H-NMR spectra for **65**, **68**, and **62**.

Pc	$\Delta H^{\ddagger}$ / kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal K^{-1} mol^{-1}	$\Delta G_{298}^{\ddagger}$ / kcal mol^{-1}	k_c/ s^{-1}	T_c/ K
			OCH_2 region		
65[a]	15.6 ± 0.7	25.6 ± 3.5	8.0 ± 1.3	418	219
68[b] (5.03 ppm)	10.1 ± 0.4	- 9.5 ± 1.5	12.9 ± 0.6	1790	288
68[b] (4.61 ppm)	10.0 ± 0.4	- 11.1 ± 1.4	13.3 ± 0.6	146	263
62[c]	13.8 ± 0.5 (A) 13.8 ± 0.5 (B)	6.8 ± 2.1 (A) 7.3 ± 2.1 (B)	11.8 ± 0.5 (A) 11.6 ± 0.5 (B)	151 (A) 192 (B)	251
			tert-Butyl region		
62[c]	13.4 ± 0.4 (A) 13.4 ± 0.4 (B)	6.2 ± 1.6 (A) 5.9 ± 1.6 (B)	11.6 ± 0.4 (A) 11.6 ± 0.4 (B)	93 (A) 73 (B)	242

[a]Equal populations, J = 0 Hz

[b]Equal populations, J = 10 Hz

[c]Unequal populations (p_A = 0.56, p_B = 0.44), J = 0 Hz

(A) and (B) refer to major and minor atropisomers respectively

T_c - coalesance temperature

K_c - coalesance rate constant

Low-Temperature ^{1}H-NMR Studies of Pcs 102 and 103

Pc **102**: Figure 17 shows the spectral changes observed in the OCH_2 region from 320 to 215 K in toluene-d_8. The room temperature spectrum displayed three sharp signals in a 1H:2H:1H ratio and one broad signal (2H). As the temperature of the sample was increased during the NMR experiment, the signal which appeared to be broad at room temperature began to split into two signals. By 320 K five well-resolved signals with an integration of 2H:2H:2H:4H:2H corresponding to the six non-equivalent neopentoxy groups were present. In contrast to this, as the temperature was decreased below room temperature, the signals began to broaden. At 270 K the ^{1}H-NMR spectrum displayed only two sharp singlets and one broad signal. Further lowering of the temperature to 255 K revealed only two sharp singlets in a 6H:2H ratio. Below 255 K the number of signals in the OCH_2 region began to increase and, by 215 K, eleven peaks were present in this region. As with the low-temperature ^{1}H-NMR spectrum obtained for the hexadecaneopentoxy phthalocyanine **68**, downfield OCH_2 signals at 6.8 and 6.32 ppm were present for this compound. However, in this case, it was not possible to see well-resolved splitting patterns.

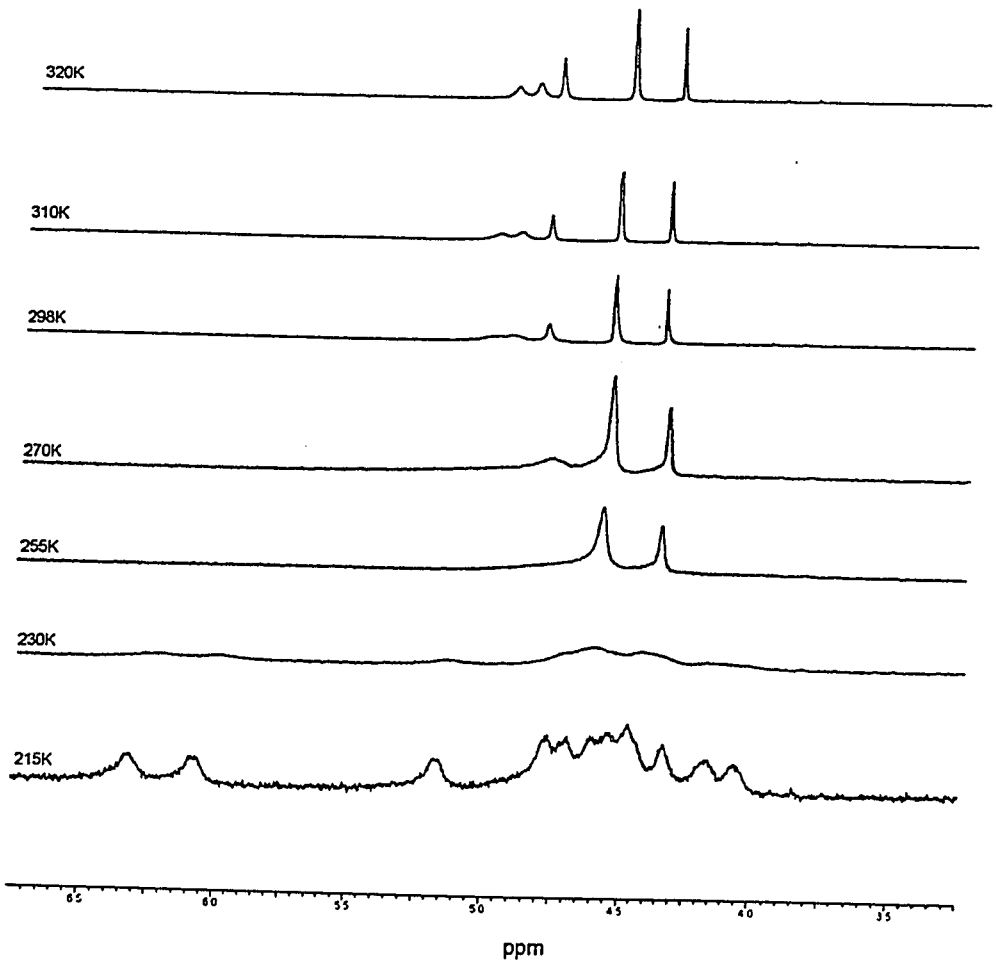


Figure 17. ^{1}H NMR spectrum of **102** in toluene-d_8 showing spectral changes in the OCH_2 region from 320 K to 215 K

Pc **103**: At room temperature, the ^{1}H-NMR for **103** displayed the expected signals in the aromatic, alkoxy and t-butyl regions of the spectrum (Figure 18). However, below room temperature, the signals in the OCH_2 region of the spectrum began to broaden and, by 265 K, one of the signals in this region had broadened into a faint bulge in the baseline. Further lowering of the temperature resulted in greater broadening of the peaks until 220 K; below this temperature, the number of signals increased. By 205 K, eight signals, corresponding to the diastereotopic OCH_2 protons, were present and, as with to the ^{1}H-NMR spectrum examined for compounds **68** and **102**, a downfield signal at 6.34 ppm was present.

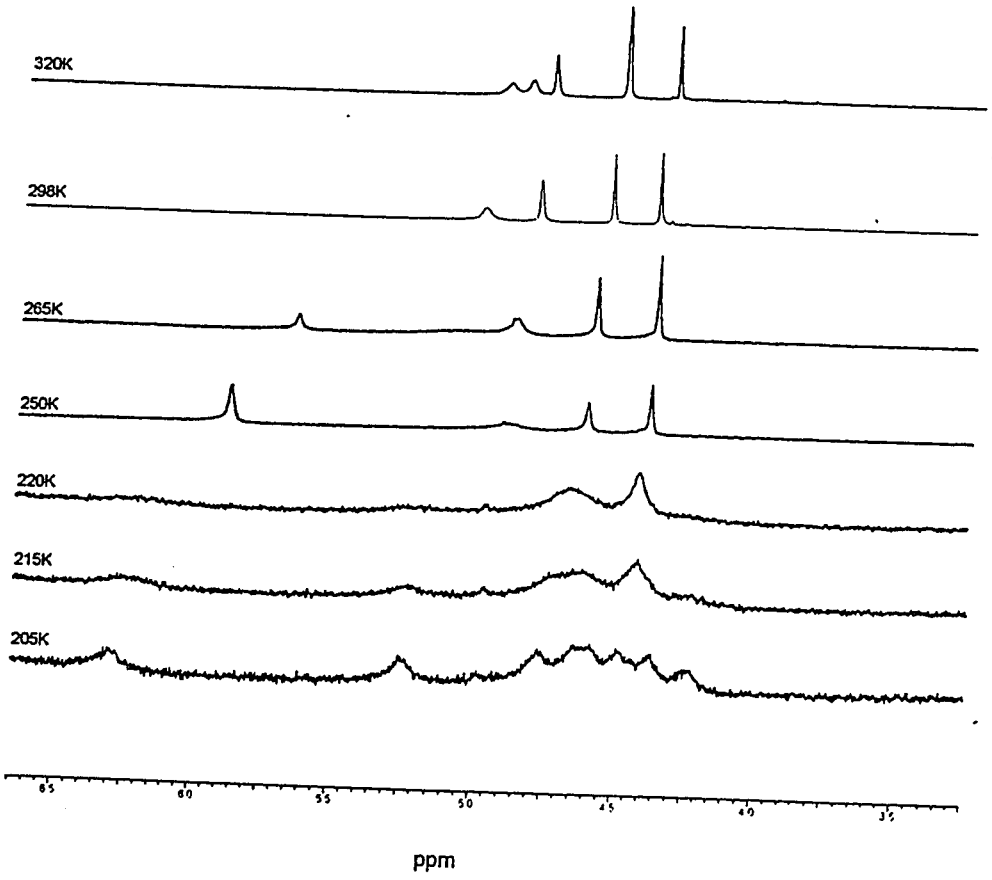


Figure 18. ^{1}H NMR spectrum of **103** in toluene-d_8 showing spectral changes in the OCH_2 region from 320 K to 205 K

CONCLUSION

A series of octa- and hexadecaneopentoxy-substituted phthalocyanines were synthesized from their corresponding 4,5-, 3,6- and 3,4,5,6-substituted phthalonitriles. The UV-Visible spectra of the highly soluble neopentoxy phthalocyanines were found to be more red-shifted than their unbranched alkoxy isomers.

A synthetic method toward the preparation of tetrasubstituted phthalonitriles was developed. Reaction of 3,4,5,6-tetrafluorophthalonitrile with morpholine or *N,N'*-methylethylenediamine gave the diaminophthalonitrile which subsequently reacted with neopentyl alcohol or 1-octanethiol to give the corresponding tetrasubstituted phthalonitriles. Self-condensation of these tetrasubstituted phthalonitriles was attempted under various conditions, but phthalocyanine formation was not observed. Alternatively, the tetrasubstituted phthalonitriles were subjected to cross-condensation reactions with phthalonitrile to afford non-centrosymmetric phthalocyanines. Surprisingly, in the reaction of 3,4,5,6-tetraneopentoxyphthalonitrile (**67**) with phthalonitrile (**3**), five different phthalocyanines were observed, despite using a large excess of phthalonitrile. Two unexpected phthalocyanines which formed were the AABB and dodeca substituted Pcs. Similarly, the reaction of a dimorpholinodithiophthalonitrile also produced the unexpected AABB substituted phthalocyanine.

In addition to this, a series of monomeric phthalocyanine intermediates were synthesized by treating phthalonitrile with morpholine or *p*-toluenesulfonyl-amide. Attempts at cross-condensation reactions between these intermediates were made. It was speculated that the tosyl group would enhance the intermediates' susceptibility towards attack by diiminoisoindoline. However, only low yields of non-centrosymmetric phthalocyanine were observed.

Furthermore, since signs of hindered rotation were discovered from the room-temperature ^{1}H-NMR spectrum of the hexadeca Pc **68**, five neopentoxy-substituted phthalocyanines were subjected to variable-temperature ^{1}H-NMR studies and the theromokinetic parameters were determined for three of these Pcs. For the octasusbstituted phthalocyanines **62** and **65**, $\Delta G^{\ddagger}$ values of 8 and 12 kcal mol^{-1}, respectively, were found whereas, for the hexadeca phthalocyanine **68**, $\Delta G^{\ddagger}$ was found to be 13 kcal mol^{-1}.

EXPERIMENTAL

General Methods

Organic solvents were dried using appropriate methods and freshly distilled before use. Inert atmosphere conditions were maintained using Matheson high purity argon. Magnetic stirring methods were utilized during reaction processes. Thin-layer chromatography (TLC) was performed using Merck silica gel 60 F_{254} polyester-backed plates and column chromatography was performed using Caledon flash grade silica gel of particle size 40-63 microns. Melting points (mp) were determined using a Kofler hot stage or a Fisher Johns melting point apparatus and are uncorrected.

Nuclear magnetic resonance (NMR) spectroscopy for proton and carbon was performed using a Bruker ARX 400 high-field Fourier Transform instrument at room temperature, unless noted otherwise. NMR spectroscopy for fluorine was recorded on a 200 MHz Bruker Aspect 3000 instrument at room temperature. Chemical shifts are reported in parts per million (δ) relative to a tetramethylsilane (TMS) internal standard for proton and carbon and relative to a fluorotrichloromethane internal standard for fluorine. The splitting patterns of proton resonances are described as singlets (s), doublets (d), doublet of doublets (dd), triplets (t) or multiplets (m). Coupling constants are reported in

Hertz for signals that are doublets, triplets and doublet of doublets. Proton decoupled chemical shifts are reported for the ^{13}C-NMR resonances.

Low temperature ^{1}H-NMR studies were performed on a Bruker ARX 400 spectrometer. ^{1}H-NMR spectra were first recorded at room temperature and then reacquired at lower temperatures in increments of five degrees. Temperatures were read directly from a thermocouple surrounding the probe. At each temperature the probe was allowed to equilibrate for about a minute before acquiring data. Test runs at longer equilibration periods (about 10 minutes) gave spectra identical to those recorded at the above conditions.

Infrared (IR) spectra were recorded on a Unicam Mattson 3000 FT-IR using KBr discs for solid samples and NaCl discs for liquid samples. Ultraviolet-visible spectra (UV-Visible) were recorded on a Hewlett-Packard HP8451A diode array spectrophotometer.

Mass spectra (MS) were recorded at 70 eV on a Kratos Profile Mass Spectrometer in the EI mode for lower molecular-weight molecules, and in the FAB mode for higher molecular-weight molecules. MALDI mass spectral analyses were performed on a PE biosystem Voyager - De™ STR Biospectrometry Workstation. High resolution mass spectrometric analyses (HRMS) were performed by Dr. K. Green at McMaster University, Hamilton, Ontario, Canada. Microanalyses were performed by Guelph Chemical Laboratory Ltd., Guelph, Ontario, Canada.

Neopentyltosylate (**59**)

A solution containing 2,2-dimethyl-1-propanol (2.9 g, 33 mmol) in 20 mL of pyridine was cooled to 0°C. To this solution, *p*-toluenesulfonyl chloride (9.5 g, 50 mmol) dissolved in 10 mL of pyridine was added dropwise over a period of 0.5 h. The reaction mixture was allowed to warm to room temperature and kept at this temperature for 2.5 h. At this time, 50 mL of water was added to quench the reaction and stirring was continued for another 0.5 h. The reaction mixture was then partitioned using 150 mL of ether and 150 mL of water. Pyridine was removed by successive washings of the ether layer with ~1M HCl solution. The ether layer was then washed with 2x150 mL of water, 2x150 mL of saturated $NaHCO_3$ solution, 2x150 mL of brine, dried over $MgSO_4$, and filtered. The ether was evaporated and the crude product was recrystallized from 95% methanol and 5% H_2O to give pure **59** in an 87% (11 g) yield: mp 44-45°C (lit. [56] mp 46.0-46.5°C); ^{1}H-NMR ($CDCl_3$): δ 7.76 (d, 2H, J = 8.4 Hz), 7.32 (d, 2H, J = 8.1 Hz), 3.63 (s, 2H), 2.42 (s, 3H), 0.87 (s, 9H); ^{13}C-NMR ($CDCl_3$): δ 144.75, 133.20, 129.91, 127.97, 79.59, 31.71, 26.10, 21.69.

1,2-Dineopentoxybenzene (**60**)

To a mixture of KOH (2.7 g, 41 mmol) in 15.4 mL of HMPA was added catechol (**17**) (2.3 g, 21 mmol), neopentyl tosylate (**59**) (10.0 g, 41 mmol) and 0.1 mL of

Aliquat 336. This mixture was stirred under an argon atmosphere while being heated at 90°C for 6 days. After this time, the reaction mixture was cooled to room temperature and poured onto 100 mL of water. The mixture was extracted with 3x100 mL of ether. The combined ether extracts were washed with 100 mL of water followed by 100 mL of brine, dried over $MgSO_4$ and filtered. The ether was removed under reduced pressure and the desired product was isolated by flash silica gel column chromatograph using 95% hexane and 5% ether as the eluting solvents. The desired product was obtained as a clear colorless liquid in a 91% yield. IR (KBr): ν = 3038 (w, =C-H), 1227 cm^{-1} (vs, C-O); ^{1}H-NMR ($CDCl_3$): δ 6.95(s, 4H), 3.71(s, 4H), 1.17(s, 18H); ^{13}C-NMR ($CDCl_3$): δ 149.77, 120.78, 113.50, 78.84, 32.20, 26.77; MS *m/z* (relative intensity): 250 (M^+, 80), 180 (m^+-C_5H_{10}, 62), 110 (catechol$^+$, 100), 71 ($(CH_3)_3CCH_2^+$, 57). Anal. calcd. for $C_{16}H_{26}O_2$: C, 76.75; H, 10.45. Found: C, 76.73; H, 10.87.

1,2-Dineopentoxybenzene (**60**) (alternative method)

To a mixture of KOH (0.17 g, 2.5 mmol) in 2 mL of HMPA was added catechol (**17**) (0.28 g, 2.5 mmol), neopentyl iodide (**58**) (0.67 mL, 5.0 mmol) and 0.1 mL of Aliquat 336. This mixture was stirred under an argon atmosphere while being heated at 90°C for 4 days. After this time, the reaction mixture was cooled to room temperature and poured onto 100 mL of water. The mixture was extracted

with 3x100 mL of ether. The combined ether extracts were washed with 100 mL of water followed by 100 mL of brine, dried over $MgSO_4$ and filtered. The ether was removed under vacuum and the desired product was isolated by flash silica gel column chromatography using 95% hexane and 5% ether as the eluting solvents. The desired product was obtained as a colorless liquid in a 64% yield (0.4 g).

1,2-Dibromo-4,5-dineopentoxybenzene (**61**)

A stirred solution containing 1,2-dineopentoxybenzene (**60**) (1 g, 4.0 mmol) in 1.6 mL of acetic acid was cooled to 3-5°C. To this solution, bromine (0.4 mL, 8.0 mmol) dissolved in 1 mL of acetic acid was added dropwise over a period of 1 h. Bromination was induced by the addition of a crystal of iodine. After the addition of bromine was complete, the mixture was allowed to stir for an additional 20 min in the ice water bath. After this time, the ice bath was removed and stirring was continued for another 1 h as the mixture was warmed to room temperature. The reaction mixture was then partitioned using 100 mL of 1% $NaHSO_3$ solution and 100 mL of ether. Successive washings of the ether layer were carried out with 100 mL portions of 1% $NaHSO_3$ solution until the aqueous layer was colorless. The ether layer was then washed with 100 mL of 5% NaOH solution, 100 mL of H_2O, 100 mL of brine, dried over $MgSO_4$ and filtered. The ether was evaporated

and the desired product was obtained in an 87% (1.42 g) yield as a clear colorless liquid that crystallized to a white solid. mp 48-49°C; IR (KBr): ν = 3076 (w, =C-H), 1250 (vs, C-O), 650 cm^{-1} (s, C-Br); ^{1}H-NMR ($CDCl_3$): δ 7.03 (s, 2H), 3.57 (s, 4H), 1.05 (s, 18H); ^{13}C-NMR ($CDCl_3$): δ 149.49, 117.39, 114.31, 79.00, 32.13, 26.57; MS *m/z* (relative intensity): 408 (M^+, 10), 268 (dibromocatechol$^+$, 100), 71 ($(CH_3)_3CCH_2^+$, 34). Anal. calcd. for $C_{16}H_{24}Br_2O_2$: C, 47.08; H, 5.93. Found: C, 47.17; H, 6.13.

4,5-Dineopentoxyphthalonitrile(**57**)

A stirred mixture of 1,2-dibromo-4,5-dineopentoxybenzene (**61**) (0.50 g, 1.67 mmol) and CuCN (453 mg, 5.00 mmol) in 6.8 mL of DMF was refluxed for 5 h under an argon atmosphere. After this time, the reaction mixture was cooled to room temperature and 17 mL of concentrated ammonium hydroxide solution was added. The suspension was allowed to stir for an additional 15 min and then the precipitate was filtered and washed with water until the filtrate was neutral. The pure product was isolated as a white solid by flash silica gel column chromatography using 3% ether and 97% toluene, in a 61% (0.30 g) yield: mp 201-202°C. IR (KBr): ν = 3095 (w, =C-H), 2229 (s, nitrile), 1230cm^{-1} (vs, C-O); ^{1}H-NMR ($CDCl_3$): δ 7.08 (s, 2H), 3.66 (s, 4H), 1.07 (s, 18H); ^{13}C-NMR ($CDCl_3$): δ 152.81, 116.05, 115.29, 108.23, 78.92, 32.10, 26.43; MS *m/z* (relative

intensity): 300 (M^+, 87), 71 ($(CH_3)_3CCH_2^+$, 57). Anal. calcd. for $C_{18}H_{24}N_2O_2$: C, 71.97; H, 8.05; N, 9.33. Found: C, 72.24; H, 7.88; N, 9.39.

2,3,9,10,16,17,23,24-Octaneopentoxyphthalocyanine nickel (II) (**62**)

A mixture containing 4,5-dineopentoxyphthalonitrile (**57**) (200 mg, 0.667 mmol) and $NiCl_2$ (53 mg, 0.111 mmol) in 6.6 mL of DMAE was heated at reflux for 48 h. After cooling to room temperature, the reaction mixture was transferred to test tubes. Precipitation of the nickel phthalocyanine was achieved by the addition of a 90% methanol /10% water solution. The precipitate was collected by centrifugation and washed twice with methanol. Further purification of the phthalocyanine involved flash silica gel column chromatography using 20% hexane / 80% toluene as the eluting solvents. Further purification of the NiPc involved precipitation using toluene and hexane. The desired NiPc was obtained as a green solid in a 28% yield (59 mg): mp > 300°C; UV-vis λ_{max} (toluene) (log ε) 672 (5.17), 640 (4.52), 604 (4.46), 4.16 (4.37), 336 (4.59), 3.14 (4.73), 288 (4.78) nm; ^{1}H-NMR (toluene-d_8): δ 8.95 (s, 8H), 3.85 (s, 16H), 1.28 (s, 72H); FAB-MS: 1260 (M+1). Anal. calcd. for $C_{72}H_{96}N_8NiO_8$: C, 68.62; H, 7.68; N, 8.89. Found: C, 69.09; H, 8.08; N, 8.56.

2,3,9,10,16,17,23,24-Octaneopentoxyphthalocyanine (**63**)

Lithium metal (11.5 mg, 1.67 mmol) was added to 1 mL of 1-pentanol under an argon atmosphere and heated at 80°C until formation of the alkoxide was complete. To this alkoxide solution 4,5-dineopentoxyphthalonitrile (**57**) (100 mg, 0.333 mmol) was added and the temperature, was raised to 100°C. After stirring the reaction mixture for 18 h at this temperature the resulting dark green mixture was cooled to room temperature and transferred to test tubes. Precipitation of the metal free Pc was achieved by the addition of a 10% water/ 90% EtOH solution along with a few drops of concentrated HCl solution to the test tubes. The precipitate was collected by centrifugation and washed twice with methanol. Further purification involved chromatography on a silica gel column using 5% hexane / 95% toluene as the eluent. Finally, the phthalocyanine was reprecipitated from toluene and EtOH to give the product in a 22% (22 mg) yield: mp>300°C; UV-vis λ_{max} (toluene) (log ε) 702 (4.94), 662 (4.87), 294 (461) nm; ^{1}H-NMR (benzene-d_6, 300 K): δ 9.10 (s, 8H), 3.88 (s, 16H), 1.24 (s, 72H), -0.71 (s, 2H); FAB-MS: 1202 (M^+). Anal. calcd. for $C_{72}H_{98}N_8O_8$: C, 71.85; H, 8.21; N, 9.31. Found: C, 70.82; H, 8.28; N, 8.70.

3,6-Dineopentoxyphthalonitrile (**64**)

To sodium metal (151 mg, 6.56 mmol) dissolved in 5 mL of methanol was added 2,3-dicyanohydroquinone (**31**) (500 mg, 3.13 mmol) and the resulting mixture was stirred at room temperature for 2 h. After this time, the solvent was removed under reduced pressure and to the residue was added neopentyl tosylate (**58**) (2.27 g, 9.38 mmol) and 10 mL of HMPA. This was stirred at 135°C for 4 days and after cooling to room temperature, the mixture was poured onto 50 mL of water and extracted with 3x50 mL of ether. The combined organic fractions were washed with 100 mL of water followed by 100 mL of brine and then dried over $MgSO_4$. The extract was filtered and then concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography using 20% ethyl acetate and 80% hexane as the eluent. The desired product was obtained as a white solid in a 62% yield (0.58 g): mp 179-181°C; IR (KBr): ν =, 3094-2873 (s, -C-H), 2230 cm^{-1} (s, nitrile); ^{1}H-NMR ($CDCl_3$): δ 7.14 (s, 2H), 3.69 (s, 4H), 1.10 (s, 18H); ^{13}C-NMR ($CDCl_3$): δ 155.57, 118.69, 113.04, 105.06, 79.96, 32.15, 26.40; MS *m/z* (relative intensity): 300 (M^+, 20), 71 ($(CH_3)_3CCH_2^+$, 100). Anal. calcd. for $C_{18}H_{24}N_2NiO_2$: C, 71.97; H, 8.05; N, 9.33. Found: C, 72.00; H, 8.17; N, 9.36.

1,4,8,11,15,18,22,25-Octaneopentoxyphthalocyanine nickel (II) (**65**)

Compound **65** was prepared following the procedure described for the preparation of **62** but starting from 3,6-dineopentoxyphthalonitrile (**64**) (300 mg, 1 mmol), $NiCl_2$ (91.2 mg, 0.333 mmol) in 9.9 mL of DMAE. Flash silica gel column chromatography was performed using 50% hexane and 50% toluene as the eluting solvents. The desired NiPc was obtained as a green solid in a 22% (69 mg) yield: mp >300°C; UV-vis λ_{max} (toluene) (log ε) 748 (5.18), 674 (4.58), 444 (4.30), 330 (4.61), 308 (4.66) nm; ^{1}H-NMR (toluene-d_8): δ 7.37 (s, 8H), 4.38 (s, 16H), 1.20 (s, 72H); ^{13}C-NMR (benzene-d_6): δ 152.37,145.97, 127.30, 119.38, 83.41, 33.34, 26.97; FAB-MS: 1258.9 (M^+). Anal. calcd. for $C_{72}H_{96}N_8NiO_8$: C, 68.62; H, 7.68; N, 8.89. Found: C, 68.63; H, 8.00; N, 8.48.

3,4,5,6-Tetraneopentoxyphthalonitrile (**67**)

To a stirred solution containing 3,4,5,6-tetrafluorophthalonitrile (**66**) (500 mg, 2.5 mmol) in 15 mL of DMF was added neopentyl alcohol (5.5 g, 62.5 mmol) and K_2CO_3 (8.6 g, 62.5 mmol). The mixture was heated at 100°C under an argon atmosphere for 24 h. After cooling to room temperature, the reaction mixture was poured onto 50 mL of H_2O and extracted with 3x50 mL of ether. The combined organic fractions were washed with 100 mL of H_2O followed by 100 mL of brine. The extract was dried over $MgSO_4$, filtered, and concentrated under

reduced pressure. Purification of the crude product involved flash silica gel column chromatography using toluene as the eluent to give the desired product in a 65% (0.76 g) yield: mp 131-133°C; IR (KBr): ν = 2870-2957 (s, -C-H), 2232 cm^{-1} (w, =C-H); ^{1}H-NMR ($CDCl_3$): δ 3.81 (s, 8H), 1.10 (s, 18H), 1.05 (s, 18H); ^{13}C-NMR ($CDCl_3$): δ 153.00, 151.90 113.34, 104.40, 85.56, 85.17, 32.76, 32.59, 26.70, 26.64; MS *m/z* (relative intensity): 472 (M^+, 5), 332 (M^+-2(C_5H_{10}), 45), 262 (M^+-3(C_5H_{10}), 100). Anal. calcd. for $C_{28}H_{44}N_2O_4$: C, 71.15; H, 9.38; N, 5.93. Found: C, 71.15; H, 9.36; N, 6.02.

1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-Hexadecaneopentoxyphthalocyanine nickel (II) (**68**)

A mixture containing 3,4,5,6-tetraneopentoxyphthalonitrile (**67**) (200 mg, 0.424 mmol) and $NiCl_2$ (33.5 mg, 0.141 mmol) in 4.2 mL of DMAE was heated at reflux for 48 h. After cooling the reaction mixture to room temperature the phthalocyanine was precipitated with 50 mL of brine, washed with 50 mL of H_2O, followed by 50 mL of methanol and then oven dried at 90°C. The precipitate was further purified by flash silica gel column chromatography using 75% hexane and 25% toluene as the eluting solvents to give the desired NiPc as a green solid in a 15 % (30 mg) yield: mp>300°C; UV-vis λ_{max} (toluene) (log ε) 758 (5.19), 676 (4.51), 440 (4.25), 386 (4.44), 342 (4.46), 314 (4.69) nm; ^{1}H-NMR (toluene-d_8

298 K): δ 4.55 (s, 2H), 1.39 (s, 9H), 1.22 (s, 9H); ^{13}C-NMR (toluene-d_8 298 K): δ 149.5, 147.30, 145.37, 123.52, 88.89, 86.88, 34.12, 33.92; FAB-MS: 1948 (M+1). Anal. calcd. for $C_{112}H_{176}N_8NiO_{16}$: C, 69.01; H, 9.10; N, 5.75. Found: C, 69.02; H, 9.29; N, 5.51.

3,4,5,6-Tetramorpholinophthalonitrile (**73**)

A stirred solution containing 3,4,5,6-tetrafluorophthalonitrile (100 mg, 0.5 mmol) in 6.25 mL of morpholine was refluxed under an argon atmosphere for 24 h. After cooling to room temperature, hexane was added to the reaction mixture and the resulting precipitate was collected by filtration. This crude product was purified by flash silica gel column chromatography using 3% CH_3OH / 97 % $CHCl_3$ as the eluent. The product was obtained as a yellow colored solid in a 68% yield (160 mg). mp 260°C (dec.); IR (KBr): ν = 2969-2855 (s, -C-H), 2224 cm^{-1} (s, CN); ^{1}H-NMR ($CDCl_3$): δ 3.92-3.88 (m, 16H), 3.31 (br, 8H), 3.2 (br, 8H); ^{13}C-NMR ($CDCl_3$): δ 156.91, 154.40, 115.88, 114.78, 67.25, 67.18, 51.61, 51.13; MS *m/z* (relative intensity): 468 (M^+, 100). Exact Mass calcd. For $C_{24}H_{32}N_6O_4$: 468.248; found 468.248.

Attempted synthesis of 1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-hexadecamorpholinophthalocyanine nickel (II)

Method A

Li (7.49 mg, 1.07 mmol) was added to 0.63 mL of 1-octanol under an argon atmosphere and heated to 80°C until all of the Li reacted. To this alkoxide solution 3,4,5,6-tetramorpholinophthalonitrile (**73**) (100 mg, 0.214 mmol) was added and the temperature was raised to 100°C. The reaction mixture was heated for 2 d at this temperature. Phthalocyanine formation was not observed as determined an UV-Visible reaction probe.

Method B

A mixture containing 3,4,5,6-tetramorpholinophthalonitrile (**73**) (160 mg, 0.342 mmol) and $NiCl_2$ (27.1 mg, 0.114 mmol) in 3.4 mL of DMAE was heated at reflux for 48 h. Phthalocyanine formation was not observed as determined an UV-Visible reaction probe.

Method C

To 2.1 mL of DMAE was added 3,4,5,6-tetramorpholinophthalonitrile (**73**) (100 mg, 0.214 mmol), the resulting mixture was heated at reflux as gaseous NH_3 was bubbled through for 12 h. UV-Visible reaction probe did not reveal any Q-band absorption peaks.

Attempted synthesis of 4,5-dimorpholinophthalonitrile (**75**)

A mixture of 4,5-dichlorophthalonitrile (**74**) (100 mg, 0.508 mmol) and morpholine (0.27 mL, 3.05 mmol) in 2 mL of DMF was stirred at 90°C. Additional K_2CO_3 was added four times in 0.5 g portions (once every 30 min for a total of 2.1 g). Heating at this temperature was continued for 2 days. After this time, the mixture was cooled to room temperature and poured on to 25 mL of water and extracted with 3x25 mL portions of ether. The combined organic fractions were washed with 25 mL of water followed by 25 mL of brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was chromatographed on a flash silica gel column using 1% CH_3OH / 99% $CHCl_3$. Compounds **75-77** were obtained in trace amounts and partially characterized by ^{1}H-NMR spectroscopy.

Compound **75**: ^{1}H-NMR ($CDCl_3$): δ 7.17 (s, 2H), 3.85 (t, 8H, J = 4.5 Hz), 3.25 (t, 8H, J = 4.6 Hz).

Compound **76**: ^{1}H-NMR ($CDCl_3$): δ 7.73 (s, 1H), 7.28(s, 1H), 3.87 (t, 4H, J = 4.3 Hz), 3.19 (t, 4H, J = 4.3 Hz).

Compound **77**: ^{1}H-NMR ($CDCl_3$): δ 7.60 (d, 1H, J = 9.0 Hz), 7.13 (d, 1H, J = 2.6 Hz), 7.04 (dd, 1H, J = 8.9 Hz, J = 2.7 Hz), 3.87 (t, 4H, J = 4.9 Hz), 3.34 (t, 4H, J = 4.9 Hz).

4-Morpholino-3,5,6-trifluorophthalonitrile (**78**)

To 3 mL of DMF was added 3,4,5,6-tetrafluorophthalonitrile (**66**) (100 mg, 0.5 mmol), morpholine (0.044 mL, 0.5 mmol) and K_2CO_3 (69.0 mg, 0.5 mmol). The resulting mixture was stirred at room temperature for 1 h and then poured onto 25 mL of water. The crude product was extracted with 3x25 mL portions of $CHCl_3$. The combined organic fractions were washed with 25 mL of brine, dried over $MgSO_4$, and filtered. Evaporation of the solvent gave a yellow solid that was recrystallized from CH_2Cl_2/hexane to give the desired product in a 67% (90 mg) yield: mp 99-100°C; IR (KBr): ν = 2969-2863 (s, -C-H), 2236 (s, CN), 1607 cm^{-1} (s, Ar); ^{1}H-NMR ($CDCl_3$): δ 3.18 (s, 4H), 3.42 (t, 4H, J = 4.6 Hz); ^{19}F-NMR ($CDCl_3$): δ -117.84 (dd, 1F, J = 16.2 Hz, 9.7 Hz), -132.02 (dd, 1F, J = 21.1 Hz, 9.7 Hz), -137.39 (t, 1F, J = 18.6 Hz); MS *m/z* (relative intensity): 267 (M^+, 75). Anal. calcd. for $C_{12}H_8F_3N_2O$: C, 53.94; H, 3.02; N, 15.73. Found: C, 53.65; H, 3.04; N, 15.53.

3,6-Difluoro-4,5-dimorpholinophthalonitrile (**81**)

A mixture of 3,4,5,6-tetrafluorophthalonitrile (**66**) (100 mg, 0.5 mmol), morpholine (43.6 mg, 0.5 mmol) and K_2CO_3 (69.0 mg, 0.5 mmol) in 3 mL of DMF were stirred at room temperature for 1 h. At this time a second equivalent of K_2CO_3

(69.0 mg, 0.5 mmol) and morpholine (43.6 mg, 0.5 mmol) were added and the mixture was allowed to stir for an additional 3 days. After this time the mixture was poured onto 25 mL of water and extracted with 3x25 mL portions of $CHCl_3$. The combined organic fractions were washed with brine, dried over $MgSO_4$, and then filtered. Evaporation of the solvent gave a yellow residue that was crystallized from ethanol to give compound **81** in a 65% (108 mg) yield: mp 235-237°C; IR (KBr): ν = 2973-2866 (vs, -C-H), 2232 (vs, nitrile), 1577 cm^{-1} (vs, Ar); ^{1}H-NMR ($CDCl_3$): δ 3.82 (t, 8H, J = 4.5 Hz), 3.29 (t, 8H, J = 4.3 Hz); ^{19}F-NMR ($CDCl_3$): δ -114.59 (s, 2H); MS *m/z* (relative intensity): 334 (M^+, 100). Anal. calcd. for $C_{16}H_{16}F_2N_4O_2$: C, 57.48; H, 4.82; N, 16.67. Found: C, 57.10; H, 4.93; N, 16.71.

1,4,8,11,15,18,22,25-Octafluoro-2,3,9,10,16,17,23,24-octamorpholino-phthalocyanine nickel (II) (**82**)

Using a mortar and pestle, 3,6-difluoro-4,5-dimorpholinophthalonitrile (**81**) (100 mg, 0.30 mmol) and $Ni(OAc)_2$ (19.0 mg, 0.075 mmol) were finely ground and transferred to a pressure bottle. After flushing with argon the pressure bottle was sealed and heated to 245°C for 6 h. Upon cooling to room temperature a dark brown crystalline solid was obtained. This crude product was chromatographed on a flash silica gel column using 95% $CHCl_3$ and 5% CH_3OH. Final purification

involved precipitation from benzene/hexane to give **82** in a 13% yield; mp>300°C; ^{1}H-NMR ($CDCl_3$): δ 4.06 (s, 32H), 3.66 (s, 32H); ^{19}F-NMR ($CDCl_3$): δ -272.06; MALDI: 1359.4 (M^+).

4,5-Dimorpholino-3,6-dineopentoxyphthalonitrile (**83**)

A mixture of 3,6-difluoro-4,5-dimorpholinophthalonitrile (**81**) (200 mg, 0.60 mmol), K_2CO_3 (1.0 g, 7.19 mmol) and neopentyl alcohol (635 mg, 7.19 mmol) in 3.6 mL of DMF was stirred at 90°C for 3 days. After cooling to room temperature, the mixture was poured onto 25 mL of water and the crude product was extracted with 3x25 mL of $CHCl_3$. The combined organic fractions were washed with brine, dried over $MgSO_4$, and then filtered. After removing the solvent under reduced pressure the crude product was crystallized from ethanol as yellow crystals (182 mg) in a 65% yield: mp 257-260°C; IR (KBr): ν = 2959-2859 (vs, -C-H), 2225 cm^{-1} (vs, nitrile); ^{1}H-NMR ($CDCl_3$): δ 3.86 (s, 4H), 3.83 (t, 8H, J = 4.4 Hz), 3.22 (t, 8H, J = 4.3 Hz), 1.16 (s, 18H); ^{13}C-NMR ($CDCl_3$): δ 157.66, 148.69, 113.74, 106.86, 85.89, 67.42, 51.03, 32.81, 27.10; MS *m/z* (relative intensity): 470 (M^+, 40). Anal. calcd. for $C_{26}H_{38}N_4O_4$: C, 66.36; H, 8.14; N, 11.91. Found: C, 66.62; H, 8.35; N, 12.10.

4,5-Dimorpholino-3,6-dioctylthiophthalonitrile (**85**)

A mixture of 3,6-difluoro-4,5-dimorpholinophthalonitrile (**81**) (200 mg, 0.60 mmol), K_2CO_3 (182 mg, 1.32 mmol) and 1-octanethiol (0.23 mL, 1.32 mmol) in 3.6 mL of DMF was stirred at 100°C for 3 h. After cooling to room temperature, the mixture was poured into 25 mL of water and the crude product was extracted with 3x25 mL of $CHCl_3$. The combined organic fractions were washed with brine and dried over $MgSO_4$. After evaporating the solvent, the crude product was crystallized from hot ethanol as yellow colored crystals (270 mg) in a 77% yield: mp 82-83°C; IR (KBr): ν = 2956-2851 (vs, -C-H), 2218 cm^{-1} (s, nitrile); ^{1}H-NMR ($CDCl_3$): δ 3.88 (t, 8H, J = 4.4 Hz), 3.31 (br, 8H), 3.09 (t, 4H, J = 7.6 Hz), 1.70-1.63 (m, 4H), 1.44-1.39 (m, 4H), 1.32-1.27 (m, 16H), 0.88 (t, 6H, J = 6.7 Hz); ^{13}C-NMR ($CDCl_3$): δ 156.74, 143.83, 120.37, 114.92, 67.14, 51.23, 37.54, 29.70, 29.11, 28.81, 22.61, 14.07; MS *m/z* (relative intensity): 586 (M^+, 10). Anal. calcd. for $C_{32}H_{50}N_4O_2S_2$: C, 65.49; H, 8.59; N, 9.55. Found: C, 65.97; H, 8.87; N, 9.22.

Attempted synthesis of 2,3,9,10,16,17,23,24-octamorpholino-1,4,8,11,15,18,22,25-octakis(octylthio)phthalocyanine nickel

Method A

Li (3.0 mg, 0.427 mmol) was added to 0.25 mL of 1-octanol under an argon atmosphere and heated to 80°C until all of the Li reacted. To this alkoxide

solution 4,5-dimorpholino-3,6-dioctylthiophthalonitrile (**85**) (50 mg, 0.085 mmol) was added and the temperature was raised to 100°C. The reaction mixture was heated for 2 days at this temperature. Phthalocyanine formation was not observed, as determined by UV-Visible reaction probes.

Method B

A mixture containing 4,5-dimorpholino-3,6-dioctylthiophthalonitrile (**85**) (100 mg, 0.171 mmol) and $NiCl_2$ (15.6 mg, 0.057 mmol) in 1.7 mL of DMAE was heated at reflux for 48 h. A small amount of Pc had formed as determined by an UV-Visible reaction probe. After cooling to room temperature, the reaction mixture was transferred to test tubes. Precipitation of the nickel phthalocyanine was attempted by adding a 90% methanol and 10% water solution. Isolation of the phthalocyanine was not possible.

Attempted synthesis of 2,3,9,10,16,17,23,24-octamorpholino-1,4,8,11,15,18,22,25-octaneopentoxyphthalocyanine nickel

Method A

Li (3.8 mg, 0.55 mmol) was added to 0.32 mL of 1-octanol under an argon atmosphere and heated to 80°C until all of the Li reacted. To this alkoxide solution 4,5-dimorpholino-3,6-dineopentoxyphthalonitrile (**83**) (50 mg, 0.11 mmol) was added and the temperature was raised to 100°C. The reaction mixture was

heated for 2 days at this temperature. Phthalocyanine formation was not observed as determined by an UV-Visible reaction probe.

Method B

A mixture containing 4,5-dimorpholino-3,6-dineopentoxyphthalonitrile (**83**) (50 mg, 0.11 mmol) and $NiCl_2$ (9.0 mg, 0.036 mmol) in 1.0 mL of DMAE was heated at reflux for 48 h. Phthalocyanine formation was not observed as determined by an UV-Vis reaction probe.

6,7-Dicyano-5,8-difluoro-2,3-dihydro-1,4-dimethylquinoxaline (**86**)

A mixture of 3,4,5,6-tetrafluorophthalonitrile (**66**) (100 mg, 0.5 mmol), K_2CO_3 (138 mg, 1.0 mmol) and N,N'-dimethylethylenediamine (0.053 mL, 0.5 mmol) was added to 3 mL of DMAE. After this time, the reaction mixture was poured onto 25 mL of water and extracted with 3x25 mL portions of $CHCl_3$. The combined organic fractions were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the resulting yellow residue was recrystallized from ethanol to give **86** (75 mg) in a 60% yield: mp 159-161°C; IR (KBr): ν = 2963-2834 (s,-C-H), 2226 (vs, nitrile), 1592 cm^{-1} (vs, Ar); ^{1}H-NMR ($CDCl_3$): δ 3.19 (s, 4H), 3.10 (s, 6H); ^{19}F-NMR ($CDCl_3$): δ -121.09;

MS *m/z* (relative intensity): 248 (M^+, 100), 233 (M^+-CH3, 37). Anal. calcd. for $C_{12}H_{10}F_2N_4$: C, 58.06; H, 4.06; N, 22.57. Found: C, 58.22; H, 4.23; N, 22.74.

6,7-Dicyano-2,3-dihydro-1,4-dimethyl-5,8-dioctylthioquinoxaline (**88**)

A mixture of compound **86** (200 mg, 0.8 mmol), K_2CO_3 (225 mg, 1.6 mmol) and 1-octanethiol (0.28 mL, 1.6 mmol) in 8 mL of DMF was stirred under an argon atmosphere for 2 days at 100°C. After this time, the reaction mixture was cooled to room temperature and poured onto 25 mL of water and extracted with 3x25 mL portions of $CHCl_3$. The combined organic fractions were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure. The resulting yellow residue was chromatographed on a flash silica gel column using 90% hexane/ 10% ethyl acetate. Compound **88** was obtained as a yellow oil (250 mg), which solidified after several days, in a 63% yield: mp 38-39°C; IR (KBr): ν = 2920-2851 (s, -C-H), 2209 cm^{-1} (s, nitrile); ^{1}H-NMR ($CDCl_3$): δ 3.21 (s, 4H), 3.09 (s, 6H), 2.96 (t, 4H, J = 7.2 Hz), 1.53-1.45 (m, 4H), 1.39-1.37 (m, 4H), 1.30-1.25 (m, 16H), 0.89 (t, 6H, J = 6.7 Hz)l; ^{13}C-NMR ($CDCl_3$): δ 146.81, 129.93, 115.87, 115.45, 47.44, 43.99, 35.30, 31.77, 29.27, 29.12, 28.54, 22.61, 14.06; MS *m/z* (relative intensity): 500 (M^+, 100). Exact Mass calcd. for $C_{28}H_{44}N_4S_2$: 500.301; found: 500.300.

4,5-Dimethoxyphthalonitrile (**91**)

Compound **91** was synthesized according to a literature procedure [97].

5,6-Dimethoxy-3-tosylimino-1-oxoisoindoline (**92**)

To 4 mL of dry methanol was added Li metal (1.8 mg, 0.27 mmol) and 4,5-dimethoxyphthalonitrile (**91**) (50 mg, 0.27 mmol). This mixture was stirred at 60°C for 2.5 h and then cooled to room temperature. The solvent was removed under reduced pressure and to the residue was added 4 mL of dry CH_2Cl_2 and *p*-toluenesulfonyl chloride (0.51 g, 2.7 mmol). The resulting mixture was stirred at room temperature for 14 h and then filtered. The filtrate was concentrated under reduced pressure and the residue was washed thoroughly with hexane. Further purification of the residue was carried out on preparative silica gel TLC plates using 10% THF/ 90% benzene as the eluent. The title compound was obtained as a yellow solid (54 mg) in a 56% yield: mp 242-244°C; IR (KBr): ν = 3405 (vs, NH), 1756 (vs, C=O), 1159 cm^{-1} (vs, O=S=O); ^{1}H-NMR ($CDCl_3$): δ 9.53 (s, 1H), 7.93 (d, 2H, J = 8.4 Hz), 7.37 (d, 2H, J = 8 Hz), 7.31 (s, 1H), 7.30 (s, 1H), 4.01 (s, 3H), 3.98 (s, 3H), 2.45 (s, 3H); ^{13}C-NMR ($CDCl_3$): δ 167.32, 157.80, 154.57, 154.17, 144.59, 136.97, 129.81, 128.79,127.38, 122.94, 105.77,105.74, 56.74, 56.70, 21.70; FAB-MS *m/z* (relative intensity): 361 (M+1, 100). Anal.

calcd. for $C_{17}H_{16}N_2O_3S$: C, 56.66; H, 4.47; N, 7.77. Found: C, 57.05; H, 4.40; N, 7.77.

5,6-Dimethoxy-3-tosylimino-1-oxoisoindoline (**92**) (alternative method)

To 2 mL of dry CH_2Cl_2 was added sodium *tert*-butoxide (51 mg, 0.53 mmol) and 4,5-dimethoxyphthalonitrile (**91**) (50 mg, 0.27 mmol). This mixture was stirred at 40°C for 4 days and then cooled to room temperature. After this time *p*-toluenesulfonyl chloride (0.25 g, 1.33 mmol) was added and the reaction mixture was stirred at room temperature for 14 h and then filtered. The filtrate was concentrated under reduced pressure and the residue was washed thoroughly with hexane. Further purification of the residue was carried out on preparative silica gel TLC plates using 10% THF and 90% benzene as the eluent. The title compound was obtained as a yellow solid (41 mg) in a 42% yield.

3-Tosylimino-1-oxoisoindoline (**93**)

To 30 mL of isopropyl alcohol was added sodium isopropoxide (0.44 g, 5.9 mmol) and phthalonitrile (**3**) (0.5 g, 3.9 mmol). This mixture was heated at 35°C until all of the phthalonitrile had reacted. At this point the solvent was removed under reduced pressure and to the residue was added 30 mL of dry CH_2Cl_2 and *p*-toluenesulfonyl chloride (1.49 g, 7.8 mol). The resulting mixture was stirred at

room temperature for 14 h and then filtered. The filtrate was concentrated under reduced pressure and the residue was washed thoroughly with hexane. Further purification of the residue involved chromatography on preparative silica gel TLC plates using 10% THF and 90% benzene as the eluent. The title compound was obtained as a yellow solid (0.80 g) in a 68% yield: mp 169-171°C; IR (KBr): ν = 3369 (vs, NH), 1758 (vs, C=O), 1156 cm^{-1} (vs, O=S=O); ^{1}H-NMR ($CDCl_3$): δ 9.75 (s, 1H), 7.92 (d, 2H, J = 8.1 Hz), 7.88 (br,1H), 7.87 (br, 1H), 7.76-7.68 (m, 2H), 7.35 (d, 2H, J = 8.1 Hz), 2.44 (s, 3H); FAB-MS: 301 (M+1). Anal. calcd. for $C_{15}H_{12}N_2O_3S$: C, 59.99; H, 4.03; N, 9.33. Found: C, 59.22; H, 3.79; N, 9.17.

5,6-Dimethoxy-1-imino-3-morpholinoisoindolenine (**94**)

To a stirred solution containing sodium metal (12.6 g, 0.546 mmol) dissolved in 2 mL of methanol was added morpholine (0.1 mL, 1.15 mmol) and 4,5-dimethoxy phthalonitrile (**91**) (100 mg, 0.532 mmol). The reaction mixture was refluxed for 3 h under an argon atmosphere and then cooled to room temperature. The precipitate that formed upon cooling was filtered, washed thoroughly with methanol, and dried to give the desired product (119 mg) in an 81% yield: mp 300°C (turns green at 193°C); IR (KBr): ν = 3250 (w, NH), 1642 (s, C=N), 1551 cm^{-1} (vs, C=N); ^{1}H-NMR ($CDCl_3$): δ 7.55 (s, 1H), 7.08 (s, 1H), 4.03 (t, 4H, J = 4.9

Hz), 4.00 (s, 3H), 3.96 (s, 3H), 3.89 (t, 4H, J = 4.9 Hz); ^{13}C-NMR ($CDCl_3$): δ 171.67, 169.15, 151.69, 150.47, 135.62, 127.44, 127.44, 106.47, 105.69, 66.60, 56.68, 56.34, 47.21; FAB-MS: 276 (M+1). Anal. calcd. for $C_{14}H_{17}N_3O_3$: C, 61.08; H, 6.22; N, 15.26. Found: C, 60.63; H, 6.22; N, 14.96.

5,6-Dineopentoxy-1-imino-3-morpholinoisoindolenine (**95**)

Compound **95** was prepared following the procedure described for the preparation of the **94** but starting from 4,5-dineopentoxyphthalonitrile (**57**) (200 mg, 0.667 mmol), sodium metal (15.3 mg, 0.667 mmol) and morpholine (0.12 mL, 0.667 mmol) in 2.8 mL of methanol. The desired product (189 mg) was obtained in a 73% yield: mp 148-150°C; IR (KBr): ν = 3203 (s, NH), 1646 (s, C=N), 1542 cm^{-1} (vs, C=N); ^{1}H-NMR ($CDCl_3$): δ 8.42 (s, 1H), 7.48 (s, 1H), 7.00 (s, 1H), 4.01 (t, 4H, J = 4.8 Hz), 3.88 (t, 4H, J = 4.8 Hz), 3.74 (s, 2H), 3.65 (s, 2H), 1.09 (s, 9H), 1.07 (s, 9H); ^{13}C-NMR ($CDCl_3$): δ 171.87, 169.38, 152.28, 150.72, 135.41, 126.90, 108.18,106.57, 79.55, 78.76, 66.64, 47.18, 32.30, 32.00, 26.62, 26.56; FAB MS *m/z* (relative intensity): 387 (M +1, 100).

5,6-Dimethoxy-1-tosylimino-3-morpholinoisoindolenine (**96**)

A mixture containing **94** (100 mg, 0.364 mmol), *p*-toluenesulfonylamide (62.2 mg, 0.364 mmol) and 0.1 mL of morpholine in 1.5 mL of methanol was stirred under

an argon atmosphere for 48 h at room temperature. After this time the methanol was removed under reduced pressure and the desired product was precipitated as a yellow solid (117 mg) from chloroform/hexane in a 75% yield: mp 225-227°C; ^{1}H-NMR ($CDCl_3$): δ 7.98 (d, 2H, J = 8.1 Hz), 7.35 (s, 1H), 7.27-7.25 (d, 2H, J = 8.1 Hz), 7.05 (s, 1H), 4.13 (t, 2H, J = 4.8 Hz), 4.09 (t, 2H, J = 4.8 Hz), 3.96 (s, 3H), 3.95 (s, 3H), 3.90 (t, 2H, J = 4.8 Hz), 3.84 (t, 2H, J = 4.8 Hz), 2.42 (s, 3H); ^{13}C-NMR ($CDCl_3$): δ 172.18, 171.07, 152.50, 151.25, 142.46, 139.93, 136.92, 128.60, 128.25, 124.89, 107.69, 106.95, 66.55, 66.44, 56.77, 56.59, 48.59, 48.19, 21.57; FAB-MS: 430 (M +1). Anal. calcd. for $C_{21}H_{23}N_3O_5S$: C, 58.73; H, 5.40; N, 9.78. Found: C, 58.59; H, 5.22; N, 9.64.

5,6-Dineopentoxy-1-tosylimino-3-morpholinoisoindolenine (**97**)

Compound **97** was prepared following the procedure described for the preparation of the **96** but starting from (**57**) (500 mg, 1.29 mmol), *p*-toluenesulfonylamide (221 mg, 1.29 mmol) and 0.1 mL of morpholine in 5 mL of methanol. The desired product was crystallized from chloroform/hexane as a yellow solid (0.55 g) in a 78% yield: mp 270-271°C; IR (KBr): ν = 1633 (s, C=N), 1146 cm^{-1} (vs, O=S=O); ^{1}H-NMR ($CDCl_3$): δ 8.02 (d, 2H, J = 8.3 Hz), 7.36 (s, 1H), 7.27 (d, 2H, J = 8.2H), 6.98 (s, 1H), 4.15 (t, 2H, J = 4.8), 4.06 (t, 2H, J = 4.7 Hz), 3.91 (t, 2H, J = 4.7 Hz), 3.86 (t, 2H, J = 4.8 Hz), 3.72 (s, 2H), 3.65 (s, 2H),

2.43 (s, 3H), 1.10 (s, 9H), 1.09 (s, 9H); ^{13}C-NMR ($CDCl_3$): δ 172.47, 171.38, 153.10, 151.43, 142.31, 140.10, 136.85,128.56, 128.31, 124.31, 109.13, 107.94, 79.48, 78.96, 66.58, 66.42, 48.49, 48.08, 32.31, 32.00, 26.57, 26.53, 21.55; FAB-MS: 542 (M +1).

5,6-Dineopentoxy-1,3-ditosyliminoisoindoline (**98**)

Sodium metal (15.3 mg, 0.660 mmol) was added to 2 mL of freshly distilled methanol. Once formation of the alkoxide was complete, 4,5-dineopentoxy phthalonitrile (**57**) (100 mg, 0.333 mmol) and *p*-toluenesulfonamide (0.126 g, 0.733 mmol) were added to the solution. This mixture was refluxed under an argon atmosphere for 5 h. After this time, the mixture was cooled to room temperature and stirred for an additional 36 h. The precipitate was filtered, washed with methanol and then dissolved in DMSO. This solution was acidified with a few drops of ~ 1M HCl and the resulting suspension was poured onto 30 mL of H_2O and extracted with 2x50 mL of $CHCl_3$. The combined organic fractions were washed with H_2O and then brine. The extract was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification of the residue involved chromatography using silica gel TLC plates with 5% THF and 95% benzene as the eluent. The title compound, a yellow colored solid (73 mg), was obtained in a 35% yield: mp 254-255°C; IR (KBr): ν = 3359 (s, NH), 1649 (s,

C=N), 1159 cm^{-1} (vs, O=S=O); ^{1}H-NMR ($CDCl_3$): δ 11.46 (s, 1H), 7.97 (d, 4H, J = 8.5 Hz), 7.37 (d, 4H, J = 8.2 Hz), 7.18 (s, 2H), 3.64 (s, 4H), 2.44 (s, 6H), 1.04 (s, 18H); ^{13}C-NMR ($CDCl_3$): δ 157.45, 154.73, 144.64, 136.86, 129.85, 127.60, 125.88, 106.44, 79.01, 32.05, 26.48, 21.70; FAB-MS: 626 (M+1). Anal. calcd. for $C_{32}H_{39}N_3O_6S_2$: C, 61.42; H, 6.28; N, 6.71. Found: C, 61.17; H, 6.13; N, 6.51.

5,6-Dimethoxy-1,3-ditosyliminoisoindoline (**99**)

Compound **99** was prepared following the procedure described for the preparation of 5,6-dineopentoxy-1,3-ditosylaminoisoindoline (**98**) starting from 4,5-dimethoxyphthalonitrile (**91**) (100 mg, 0.53 mmol), *p*-toluenesufonamide (206 mg, 1.2 mmol), and sodium metal (25 mg 1.06 mmol) in 2 mL of methanol. The title compound (42 mg) was obtained in a 15% yield: mp 259-260°C; IR (KBr): ν = 3330 (s, NH), 1647 (s, C=N), 1159 cm^{-1} (vs, O=S=O); ^{1}H-NMR ($CDCl_3$): δ 11.55 (s, 1H), 8.00 (d, 4H, J = 7.92 Hz), 7.40 (d, 4H, J = 8.0 Hz), 7.30 (s, 2H), 3.97 (s, 6H), 2.48 (s, 6H); ^{13}C-NMR ($CDCl_3$): δ 157.08, 154.49, 144.75, 136.71, 129.88, 127.64, 126.40, 105.92, 56.75, 21.71; FAB-MS *m/z* (relative intensity): 514 (M+1). Anal. calcd. for $C_{24}H_{23}N_3O_6S_2$: C, 56.13; H, 4.51; N, 8.18. Found: C, 56.08; H, 4.24; N, 8.16.

1,3-Ditosyliminoisoindoline (**100**)

Compound **100** was prepared following the procedure described for the preparation of 5,6-dineopentoxy-1,3-ditosylaminoisoindoline (**98**) starting from phthalonitrile (**3**) (100 mg, 0.78 mmol), *p*-toluenesufonamide (294 mg, 1.7 mmol), sodium metal (36 mg, 1.6 mmol) in 2 mL of methanol. The title compound (212 mg) was obtained in a 60% yield: mp 225-227°C; IR (KBr): ν = 3332 (s, NH), 1652 (s, C=N), 1151 cm^{-1} (vs, O=S=O); ^{1}H-NMR ($CDCl_3$): δ 11.76 (s, 1H), 7.95 (d, 4H, J = 8.2 Hz), 7.86-7.84 (m, 2H), 7.66-7.64 (m, 2H), 7.35 (d, 4H, J = 8.1 Hz), 2.46 (s, 6H); ^{13}C-NMR ($CDCl_3$): δ 156.69, 144.84, 136.59, 134.35, 133.12, 129.88, 127.63,124.47, 21.68; FAB-MS *m/z* (relative intensity): 454 (M+1). Anal. calcd. for $C_{22}H_{19}N_3O_4S_2$: C, 58.25; H, 4.22; N, 9.26. Found: C, 58.41; H, 4.40; N, 9.02.

Attempted cross-condensation of 5,6-dineopentoxy-1-tosylimino-3-morpholino-isoindolenine with diiminoisoindoline

A mixture of 5,6-dineopentoxy-1-tosylimino-3-morpholinoisoindolenine (**97**) (300 mg, 0.665 mmol), and diiminoisoindoline (**4**) (96.5 mg, 0.665 mmol) in 4 mL of DMF was stirred at room temperature for 4 days under an argon atmosphere. After this time, the reaction mixture was transferred to test tubes and the phthalocyanine was precipitated by the addition of a 10% methanol and 90%

water solution. The precipitate was collected by centrifugation and washed with methanol until the filtrate was light yellow. Further purification involved chromatography on a flash silica gel column using THF as eluant.

Attempted synthesis of 2,3-dineopentoxyphthalocyanine (**101**)

A mixture of 5,6-dimethoxy-1-tosylimino-3-morpholinoisoindolenine (**96**) (100 mg, 0.233 mmol), and diiminoisoindoline (**4**) (33.8 mg, 0.233 mmol) in 1.6 mL of DMF was stirred at room temperature for 4 days under an argon atmosphere. After this time, the reaction mixture was transferred to test tubes and the phthalocyanine was precipitated by the addition of a 10% methanol and 90% water solution. The precipitate was collected by centrifugation and washed with methanol until the filtrate was light yellow. Further purification or analysis of this precipitate was not completed due to its extreme insolubility.

Attempted cross-condensation reaction using 5,6-dineopentoxy-1,3-ditosyl-iminoisoindoline (**98**)

A mixture of 5,6-dineopentoxy-1,3-ditosyliminoisoindoline (**98**) (0.083 g, 0.315 mmol), and diiminoisoindoline (0.046 g, 0.315 mmol) in 2 mL of DMF was stirred at room temperature for 4 days under an argon atmosphere. After this time, the reaction mixture was transferred to test tubes and the phthalocyanine was precipitated by the addition of a 10% methanol and 90% water solution. The

precipitate was collected by centrifugation and washed with methanol until the filtrate was light yellow. Only unsubstituted phthalocyanine was obtained.

Cross-condensation of 3,4,5,6-tetraneopentoxyphthalonitrile (**67**) with phthalonitrile (**3**)

A mixture of 3,4,5,6-tetraneopentoxyphthalonitrile (**67**) (500 mg, 1.06 mmol), phthalonitrile (**3**) (1.36 g, 10.6 mmol) and $NiCl_2$ (3.19 g, 11.7 mmol) in 14 mL of DMAE was refluxed for 48 h under an argon atmosphere. After cooling to room temperature, the reaction mixture was transferred to test tubes. Precipitation of the nickel phthalocyanine was carried out by adding a 10% methanol and 90% water solution. The precipitate was collected by centrifugation and washed with methanol until the filtrate was light yellow. The precipitate was dried, transferred to a thimble and extracted in a Soxhlet extractor using benzene. After this time, the solvent was removed under reduced pressure and the residue was chromatographed on a flash silica gel column using benzene as the eluent. All of the blue and green colored fractions were collected, combined and further chromatographed on a second flash silica gel column using 50% hexane and 50% benzene (1:1). The first fraction eluted from the column contained trace amounts of **68**, the second band contained **102** (16 mg, 3%). The third band contained **103** (20 mg, 3%) and the fourth band contained **104** (10 mg, 2%).

*1,2,3,4,8,9,10,11,15,16,17,18-dodecaneopentoxyphthalocyanine nickel (**102**)*

UV-vis λ_{max} (toluene) (log ε) 730 (4.79), 654 (4.43), 310 (4.57) nm; ^{1}H-NMR (benzene-d_6): δ 9.77-9.75 (m, 2H), 7.95-7.93 (m, 2H), 5.01 (br, 8H), 4.91 (s, 4H), 4.69 (s, 8H), 4.50 (s, 4H), 1.56 (s, 18H), 1.51 (s, 36H), 1.42 (s, 18H), 1.40 (s, 18H), 1.36 (s, 18H); ^{13}C-NMR (benzene-d_6): δ 149.24, 149.15, 149.09, 147.07, 146.53, 145.61, 145.32, 145.15, 137.69, 128.93, 124.86, 123.84, 123.73, 122.45, 88.53, 88.33, 86.43, 86.26, 85.87, 33.63, 33.54, 33.29, 33.25, 33.15, 33.03, 27.19, 27.13, 27.08, 26.87; MALDI: 1065.2(M+1).

*1,2,3,4,8,9,10,11-octaneopentoxyphthalocyanine nickel (**103**)*

UV-vis λ_{max} (toluene) (log ε) 706 (4.87), 636 (4.25), 370 (4.12), 334 (4.34), 304 (4.43) nm; ^{1}H-NMR (benzene-d_6): δ 9.63 (d, 2H, J = 7.6 Hz), 9.23 (d; 2H, J = 7.5 Hz), 7.91 (t, 2H, J = 7.3 Hz), 7.84 (t, 2H, J = 7.3 Hz), 5.20 (br, 4H), 5.01 (s, 4H), 4.75 (s, 4H), 4.58 (s, 4H), 1.62 (s, 18H), 1.56 (s, 18H), 1.49 (s, 18H), 1.45 (s, 18H); ^{13}C-NMR (benzene-d_6): δ 149.35, 149.29, 147.24, 146.77, 145.85, 145.82, 145.55, 144.78, 137.38, 137.25, 128.86, 128.73, 124.80, 123.93, 122.28, 121.74, 88.53, 86.50, 86.24, 85.85, 33.66, 33.30, 33.20, 33.07, 27.23, 27.16, 27.14, 26.95; FAB-MS: 1259 (M^+); MALDI (1258.5) (M^+).

*1,2,3,4-tetraneopentoxyphthalocyanine nickel (**104**)*

UV-vis λ_{max} (toluene) (log ε) 692 (4.91), 622 (4.39), 338 (4.34), 294 (4.36) nm; ^{1}H-NMR (benzene d_6): δ 9.75 (br, 2H), 9.52 (br, 2H), 9.46 (br, 2H), 7.99-7.87 (m, 6H), 5.02 (s, 4H), 4.55 (s, 4H), 1.65 (s, 18H), 1.59 (s, 18H); MALDI: 912.1(M^+).

Cross-condensation of 4,5-dimorpholino-3,6-dioctylthiophthalonitrile (**85**) with phthalonitrile (**3**)

A mixture of 4,5-dimorpholino-3,6-dioctylthiophthalonitrile (**85**) (500 mg, 0.853 mmol), phthalonitrile (**3**) (1.09 g, 8.53 mmol) and $NiCl_2$ (2.60 g, 9.38 mmol) in 11 mL of DMAE was refluxed for 48 h under an argon atmosphere. After cooling to room temperature, the reaction mixture was transferred to test tubes. Precipitation of the nickel phthalocyanine was carried out by adding a 10% methanol and 90% water solution. The precipitate was collected by centrifugation and washed with methanol until the filtrate was light yellow. The precipitate was dried, transferred to a thimble and extracted in a Soxhlet extractor using benzene. After this time, the solvent was evaporated and the residue was chromatographed on a flash silica gel column using 50% ethyl acetate/ 50% hexane. All of the blue and green colored fractions were collected and further chromatographed on an SX-3 Biobeads® column using toluene as the eluent. Two bands were separated and they were further chromatographed on a flash silica gel column using 50% ethyl acetate/ 50%hexane. The first band

that eluted from the SX-3 Biobeads® column contained **105** (14 mg, 2.2%), the second band contained **106** (34 mg, 4%).

*2,3,9,10-tetramorpholino-1,4,8,11-tetraoctylthiophthalocyanine nickel (**105**)*

UV-vis λ_{max} (toluene) (log ε) 714 (4.86), 642 (4.25), 336 (4.58), 308 (4.62) nm; ^{1}H-NMR (benzene-d_6): δ 9.64 (d, 2H, J = 7.5 Hz), 9.13 (d, 2H, J = 7.4 Hz), 8.02 (t, 2H, J = 7.3 Hz), 7.78 (t, 2H, J = 7.3 Hz), 4.42 (s, 8H), 4.33 (s, 2H), 4.04 (br, 16H), 3.90 (t, 4H, J = 7.1 Hz), 3.74 (t, 4H, J = 7.4 Hz), 2.03-1.88 (m, 8H), 1.47-1.37 (m, 16H), 1.15-0.99 (m, 24H), 0.80 (t, 6H, J = 6.7 Hz), 0.74 (t, 6H, J = 7.0 Hz); ^{13}C-NMR (benzene-d_6): δ 155.16, 154.31, 146.13, 146.15, 145.45, 145.16, 144.23, 137.99, 137.81, 137.13, 136.26, 135.41, 129.63, 129.22, 122.52, 121.78, 67.87, 67.78, 52.25, 39.66, 38.51, 31.77, 30.53, 29.97, 29.45, 29.40, 29.34, 29.24, 29.19, 22.59, 22.56, 13.91, 13.85; FAB-MS: 1488 (M+1); MALDI: (1487.9) (M+1).

*2,3-dimorpholino-1,4-dioctylthiophthalocyanine nickel (**106**)*

UV-vis λ_{max} (toluene) (log ε) 684 (4.91), 620 (4.31), 336 (4.65), 300 (4.69) nm; ^{1}H-NMR (benzene-d_6): δ 9.29 (d, 2H, J = 7.5 Hz), 8.61 (d, 2H, J = 7.3 Hz), 8.38 (br, 2H), 7.86 (t, 2H, J = 7.1 Hz), 7.65 (t, 2H, J = 7.1 Hz), 7.35 (br, 2H), 4.43 (s, 8H), 4.03 (s, 8H), 3.85 (t, 4H, J = 7.3 Hz), 2.13-2.05 (m, 4H), 1.64-1.59 (m, 4H),

1.33-1.21 (m, 12H), 1.01 (m, 4H), 0.83 (t, 6H, J = 6.8); FAB-MS: 1030 (M+1); MALDI (1029.4) (M^+).

Attempted cross-condensation of 4,5-dimorpholino-3,6-dioctylthiophthalonitrile (**85**) with phthalonitrile (**3**) (dimeric intermediate)

Sodium metal (2.0 mg, 0.085 mmol) was added to 2 mL of methanol under an argon atmosphere and stirred at room temperature until all of the sodium reacted. To this alkoxide solution was added 4,5-dimorpholino-3,6-dioctylthiophthalonitrile (**85**) (100 mg, 0.17 mmol) and the mixture was heated at reflux overnight. After cooling to room temperature, the methanol was evaporated. Phthalonitrile (**3**) (218 mg, 1.71 mmol), $NiCl_2$ (519 mg, 1.88 mmol) and 2.2 mL of DMAE were added to the residue and the resulting mixture was heated at reflux for 91 h. After cooling to room temperature, the reaction mixture was transferred to test tubes and washed with a 10% CH_3OH / 90% H_2O solution. The precipitate was collected by centrifugation and washed several times with CH_3OH. Further purification of the precipitate was not possible due to its extreme insolubility in common organic solvents.

Attempted cross-condensation reactions of 4,5-dimorpholino-3,6-dioctylthio phthalonitrile (**85**) with 4-nitrophthalonitrile (**5**)

A mixture of 4,5-dimorpholino-3,6-dioctylthiophthalonitrile (**85**) (100 mg, 0.171 mmol), 4-nitrophthalonitrile (**5**) (295 mg, 1.71 mmol) and $NiCl_2$ (519 mg, 1.88 mmol) in 2.2 mL of DMAE was refluxed for 48 h under an argon atmosphere. After cooling to room temperature, the reaction mixture was transferred to test tubes. Precipitation of the nickel phthalocyanines was carried out by adding a 10% methanol and 90% water solution. The precipitate was collected by centrifugation and washed with methanol until the filtrate was light yellow. Purification was attempted on an SX-3 Biobeads® column using 1% TFA/ DMF as the eluants. MALDI MS did not reveal peaks corresponding to any of the desired Pcs. Further purification or analysis of this precipitate was not completed due to its extreme insolubility.

Attempted cross-condensation reactions of 4,5-dimorpholino-3,6-dioctylthiophthalonitrile (**85**) with 4-nitrophthalonitrile (**5**) (via a dimeric intermediate)

Lithium metal (5.9 mg, 0.853 mmol) was added to 1.7 mL of methanol under an argon atmosphere and stirred at room temperature until all of the lithium reacted. To this alkoxide solution was added 4-nitrophthalonitrile (**5**) (295 mg, 1.71 mmol) and the mixture was heated at reflux for 2 h. After cooling to room temperature,

the methanol was removed under reduced pressure. 4,5-dimorpholino-3,6-di octylthiophthalonitrile (**85**) (100 mg, 0.171 mmol), $NiCl_2$ (519 mg, 1.88 mmol) and 2.2 mL of DMAE were added to the residue and the resulting mixture was heated at reflux for 48 h. After cooling to room temperature, the reaction mixture was transferred to test tubes and washed with a 10% CH3OH / 90% H_2O solution. The precipitate was collected by centrifugation and washed several times with CH_3OH. Further purification of the precipitate was not possible due to its extreme insolubility in common organic solvent.

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APPENDIX

Table 3. Crystal data and structure refinement for **81**.

Identification code	**81**	
Empirical formula	C16.50 H17 Cl F2 N4 O2	
Formula weight	376.79	
Temperature	150(1) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 29.2667(12) Å	α= 90°.
	b = 6.5982(2) Å	β= 116.866(2)°.
	c = 19.0442(8) Å	γ = 90°.
Volume	3280.6(2) $Å^3$	
Z	8	
Density (calculated)	1.526 Mg/m^3	
Absorption coefficient	0.274 mm^{-1}	
F(000)	1560	
Crystal size	0.35 x 0.25 x 0.25 mm^3	
Theta range for data collection	2.95 to 27.48°.	
Index ranges	0<=h<=38, 0<=k<=8, -24<=l<=22	
Reflections collected	7835	
Independent reflections	3723 [R(int) = 0.027]	
Completeness to theta = 27.48°	98.7 %	
Absorption correction	multi-scan (Denzo-SMN)	
Max. and min. transmission	0.9346 and 0.9101	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3723 / 0 / 232	
Goodness-of-fit on F^2	1.044	
Final R indices [I>2sigma(I)]	R1 = 0.0532, wR2 = 0.1235	
R indices (all data)	R1 = 0.0856, wR2 = 0.1389	
Extinction coefficient	0.0018(4)	
Largest diff. peak and hole	0.708 and -0.796 $e.Å^{-3}$	

Table 4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **81**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
F(1)	586(1)	1710(2)	-1452(1)	27(1)
F(2)	534(1)	3177(2)	1307(1)	28(1)
O(1)	2110(1)	-323(3)	-621(1)	31(1)
O(2)	2091(1)	5383(3)	2687(1)	34(1)
N(1)	-774(1)	2550(3)	-10(1)	34(1)
N(2)	-730(1)	1714(3)	-2027(1)	34(1)
N(3)	1515(1)	2072(3)	-109(1)	24(1)
N(4)	1476(1)	3176(3)	1314(1)	25(1)
C(1)	559(1)	2732(3)	630(1)	20(1)
C(2)	99(1)	2495(3)	-37(1)	20(1)
C(3)	114(1)	2245(3)	-764(1)	21(1)
C(4)	584(1)	2164(3)	-765(1)	20(1)
C(5)	1055(1)	2325(3)	-87(1)	20(1)
C(6)	1040(1)	2730(3)	640(1)	20(1)
C(7)	-380(1)	2539(3)	-6(1)	23(1)
C(8)	-352(1)	1962(3)	-1476(1)	24(1)
C(9)	1629(1)	2760(3)	-741(1)	25(1)
C(10)	1722(1)	990(4)	-1166(1)	29(1)
C(11)	1892(1)	619(4)	422(1)	29(1)
C(12)	1956(1)	-1082(4)	-58(1)	31(1)
C(13)	1848(1)	4672(4)	1317(1)	29(1)
C(14)	1919(1)	6271(4)	1925(1)	31(1)
C(15)	1603(1)	2333(4)	2089(1)	26(1)
C(16)	1711(1)	4009(4)	2685(1)	32(1)
Cl(1)	544(1)	6507(2)	-1947(1)	87(1)
C(1S)	0	7893(6)	-2500	53(1)

Table 5. Bond lengths [Å] and angles [°] for **81**.

F(1)-C(4)	1.346(2)
F(2)-C(1)	1.355(2)
O(1)-C(12)	1.431(3)
O(1)-C(10)	1.433(3)
O(2)-C(14)	1.430(3)
O(2)-C(16)	1.432(3)
N(1)-C(7)	1.151(3)
N(2)-C(8)	1.142(3)
N(3)-C(5)	1.376(3)
N(3)-C(9)	1.460(3)
N(3)-C(11)	1.466(3)
N(4)-C(6)	1.373(3)
N(4)-C(15)	1.458(3)
N(4)-C(13)	1.466(3)
C(1)-C(2)	1.379(3)
C(1)-C(6)	1.399(3)
C(2)-C(3)	1.415(3)
C(2)-C(7)	1.429(3)
C(3)-C(4)	1.376(3)
C(3)-C(8)	1.436(3)
C(4)-C(5)	1.402(3)
C(5)-C(6)	1.430(3)
C(9)-C(10)	1.514(3)
C(11)-C(12)	1.511(3)
C(13)-C(14)	1.509(3)
C(15)-C(16)	1.513(3)
Cl(1)-C(1S)	1.721(2)
C(1S)-Cl(1)#1	1.721(2)
C(12)-O(1)-C(10)	109.81(16)

C(14)-O(2)-C(16)	109.91(17)
C(5)-N(3)-C(9)	125.31(17)
C(5)-N(3)-C(11)	120.05(18)
C(9)-N(3)-C(11)	113.02(17)
C(6)-N(4)-C(15)	124.65(18)
C(6)-N(4)-C(13)	121.48(18)
C(15)-N(4)-C(13)	113.78(17)
F(2)-C(1)-C(2)	116.80(18)
F(2)-C(1)-C(6)	118.22(18)
C(2)-C(1)-C(6)	124.69(19)
C(1)-C(2)-C(3)	117.75(18)
C(1)-C(2)-C(7)	121.79(19)
C(3)-C(2)-C(7)	120.45(19)
C(4)-C(3)-C(2)	118.52(18)
C(4)-C(3)-C(8)	121.22(19)
C(2)-C(3)-C(8)	120.16(19)
F(1)-C(4)-C(3)	116.89(18)
F(1)-C(4)-C(5)	118.51(18)
C(3)-C(4)-C(5)	124.29(19)
N(3)-C(5)-C(4)	122.14(18)
N(3)-C(5)-C(6)	120.61(18)
C(4)-C(5)-C(6)	117.24(19)
N(4)-C(6)-C(1)	121.16(19)
N(4)-C(6)-C(5)	121.59(19)
C(1)-C(6)-C(5)	117.21(18)
N(1)-C(7)-C(2)	177.4(2)
N(2)-C(8)-C(3)	177.8(2)
N(3)-C(9)-C(10)	111.39(18)
O(1)-C(10)-C(9)	110.76(17)
N(3)-C(11)-C(12)	109.24(17)
O(1)-C(12)-C(11)	111.1(2)
N(4)-C(13)-C(14)	108.58(18)

O(2)-C(14)-C(13)	110.82(19)
N(4)-C(15)-C(16)	110.59(19)
O(2)-C(16)-C(15)	111.32(18)
Cl(1)#1-C(1S)-Cl(1)	115.8(2)

Symmetry transformations used to generate equivalent atoms:
#1 -x,y,-z-1/2

Table 6. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **81**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
F(1)	25(1)	37(1)	20(1)	-4(1)	11(1)	1(1)
F(2)	28(1)	37(1)	22(1)	-2(1)	14(1)	1(1)
O(1)	29(1)	39(1)	29(1)	7(1)	17(1)	12(1)
O(2)	30(1)	39(1)	25(1)	-7(1)	6(1)	-6(1)
N(1)	28(1)	33(1)	48(1)	6(1)	22(1)	2(1)
N(2)	29(1)	41(1)	31(1)	-3(1)	12(1)	-2(1)
N(3)	20(1)	32(1)	23(1)	5(1)	12(1)	6(1)
N(4)	22(1)	34(1)	18(1)	-2(1)	8(1)	-9(1)
C(1)	24(1)	19(1)	21(1)	1(1)	13(1)	1(1)
C(2)	19(1)	18(1)	26(1)	1(1)	12(1)	1(1)
C(3)	19(1)	19(1)	22(1)	0(1)	7(1)	1(1)
C(4)	23(1)	20(1)	19(1)	-1(1)	11(1)	0(1)
C(5)	19(1)	17(1)	22(1)	1(1)	9(1)	1(1)
C(6)	22(1)	17(1)	20(1)	1(1)	9(1)	0(1)
C(7)	25(1)	19(1)	27(1)	4(1)	13(1)	2(1)
C(8)	22(1)	24(1)	27(1)	-1(1)	14(1)	1(1)
C(9)	21(1)	30(1)	26(1)	7(1)	13(1)	3(1)
C(10)	28(1)	40(1)	23(1)	5(1)	14(1)	8(1)
C(11)	24(1)	39(1)	22(1)	8(1)	9(1)	10(1)
C(12)	30(1)	33(1)	31(1)	8(1)	16(1)	10(1)
C(13)	23(1)	35(1)	27(1)	-1(1)	11(1)	-8(1)
C(14)	23(1)	32(1)	31(1)	-1(1)	7(1)	-1(1)
C(15)	24(1)	30(1)	23(1)	2(1)	9(1)	1(1)
C(16)	34(1)	39(2)	22(1)	-2(1)	12(1)	0(1)
Cl(1)	100(1)	90(1)	71(1)	39(1)	40(1)	50(1)
C(1S)	47(3)	32(2)	87(3)	0	35(2)	0

Table 7. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3)
for **81**.

	x	y	z	U(eq)
H(9A)	1936	3638	-519	30
H(9B)	1338	3576	-1121	30
H(10A)	1400	219	-1452	35
H(10B)	1830	1504	-1556	35
H(11A)	1774	66	796	34
H(11B)	2224	1306	728	34
H(12A)	2216	-2049	298	37
H(12B)	1627	-1820	-335	37
H(13A)	1721	5302	791	34
H(13B)	2179	4002	1446	34
H(14A)	2173	7281	1939	37
H(14B)	1590	6981	1777	37
H(15A)	1908	1449	2258	32
H(15B)	1314	1495	2059	32
H(16A)	1391	4761	2560	39
H(16B)	1832	3410	3216	39
H(1S1)	-70	8781	-2141	64
H(1S2)	70	8781	-2859	64