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An investigation into the ring-enlargement reactions of boron subphthalocyanine and boron subnaphthalocyanine

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AN INVESTIGATION INTO THE RING-ENLARGEMENT REACTIONS OF BORON SUBPHTHALOCYANINE AND BORON SUBNAPHTHALOCYANINE

by

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DEDICATIONS

This work is dedicated to the Lord, who gave me the talent and carried me through the tough times in research; to my wife Melissa, who supported me and encouraged me to the end; and to my parents, Ron and Val, who started me off on the fantastic voyage of chemistry.

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I would like to acknowledge the support, teaching, encouragement, and patience of Dr. Vance Kennedy, without whom I would not have succeeded. I would also like to acknowledge the entire Department of Chemistry as a great environment for young chemists to gain knowledge, deep understanding, and priceless mentoring. Finally, I would like to acknowledge the University of Michigan Technical Services Department for the mass spectral analysis.

ABSTRACT

Ring enlargement syntheses of axially substituted boron subphthalocyanine and boron subnaphthalocyanine were investigated. The trihexylsiloxy derivatives of subphthalocyanine and subnaphthalocyanine were synthesized. These derivatives were then used in the ring-enlargement trials. Symmetrical and asymmetrical ring-enlargement reactions were carried out in a mixture of toluene and dimethylsulfoxide at room temperature. This study represents the first synthesis of boron subphthalocyanine with trihexylsiloxy group in the axial position and the first investigation into the ring enlargement of boron subnaphthalocyanine in which the axial ligand is a trihexylsiloxy group. Precipitates were formed, and it is believed that the precipitates are the metal-free ring-enlarged products. Characterization by UV-Vis and high resolution mass spectroscopy offer evidence that three of the four reactions were successful.

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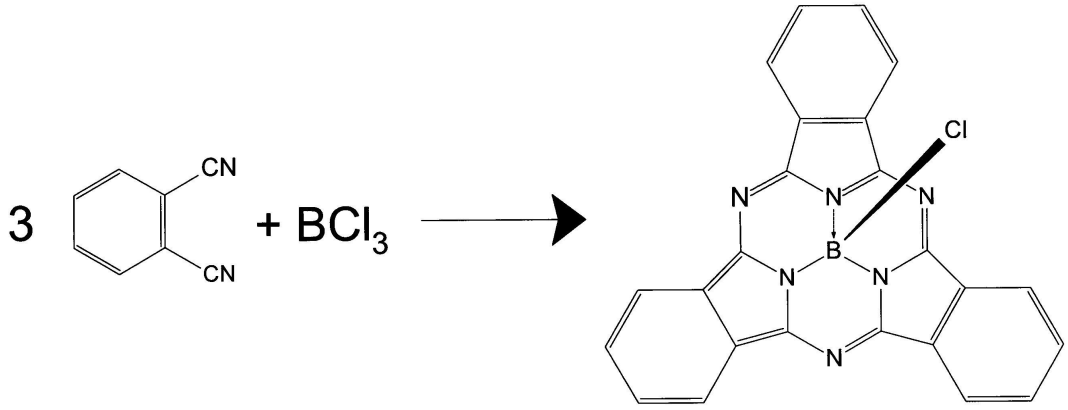
CHAPTER 1: INTRODUCTION AND BACKGROUND

The first subphthalocyanine (SubPc) was reported by Meller and Ossko when it was accidentally synthesized in 1972. The group was trying to prepare derivatives of phthalocyanines (Pc) that contained boron as the central metal by reacting phthalonitrile with haloboranes **(Scheme 1.1)**. The subphthalocyanine, chloro[subphthalocyaninato]boron(III), was reported by them[1], and a crystal structure for the compound was reported in 1974. Not until 1990 were these compounds reported again when the bromo-derivative of the t-butyl substituted macrocycle was reported by Kobayashi et al.[2]



Scheme 1.1 Synthesis of chloro[subphthalocyaninato]boron (III).

Subphthalocyanines contain a delocalized 14 π-electron system that gives rise to strong absorption bands in their visible electronic spectra (Figure 1.1). They have a strong absorption band in the near UV (Soret-like band) at 305 nm and a strong absorption (Q-like band) at 565 nm and appear red in color. The

phthalocyanines have a delocalized 18 π-electron system (Figure 1.2), the subnaphthalocyanines have a delocalized 20 π-electron system (Figure 1.3), and the naphthalocyanines have a delocalized 26 π-electron system (Figure 1.4).[3]

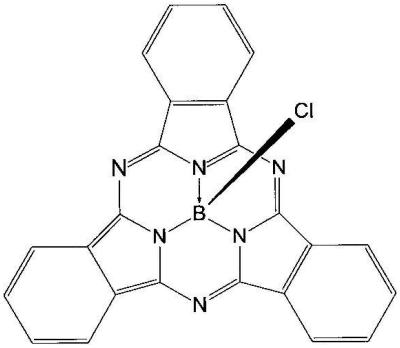


Figure 1.1 Subphthalocyanine.

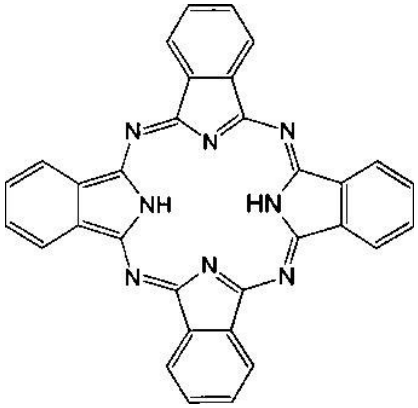


Figure 1.2 Phthalocyanine.

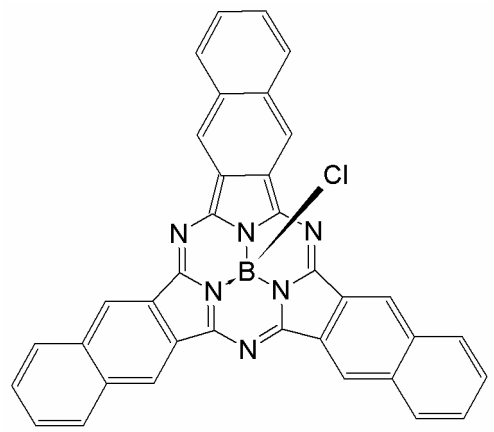


Figure 1.3 Subnaphthalocyanine.

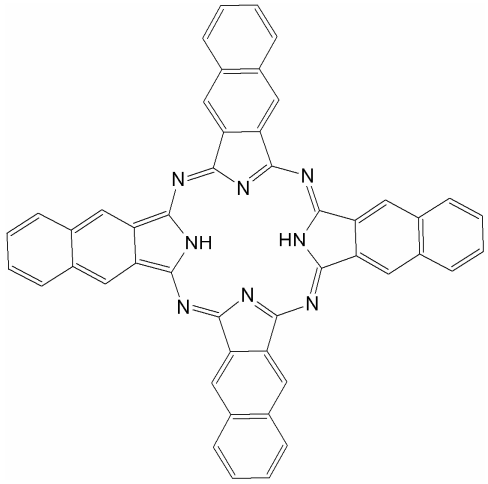


Figure 1.4 Naphthalocyanine.

The subphthalocyanines, phthalocyanines, subnaphthalocyanines, and naphthalocyanines are all brightly colored solids and also in solution. It has been determined by X-ray diffraction that the subphthalocyanines and

subnaphthalocyanines have a bowl-like shape with the axial ligand pointing in the direction opposite that of the open bowl (Figure 1.5). However, their homologues, the phthalocyanines and naphthalocyanines, are typically planar, with the axial ligands at right angles to the plane of the molecule (Figure 1.6).[4]

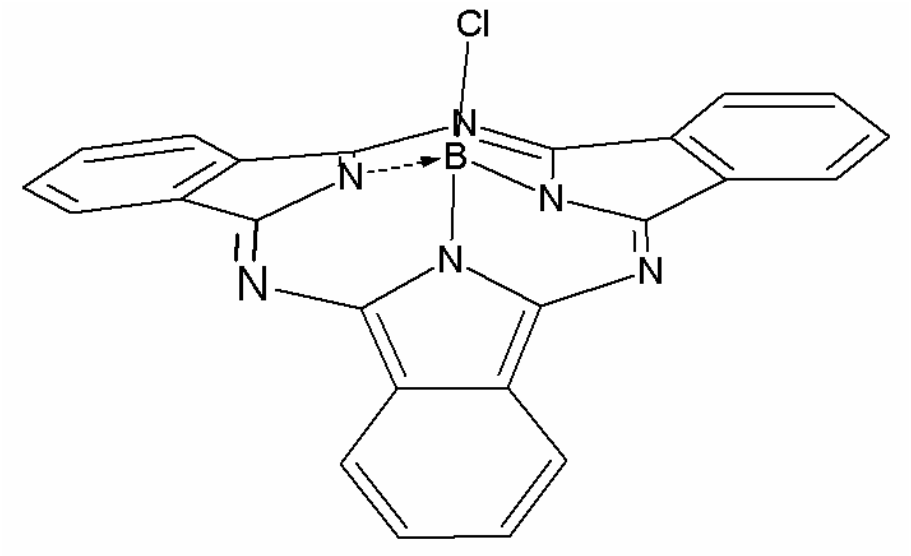


Figure 1.5 3-D representation of chloro[subphthalocyaninato]boron (III).

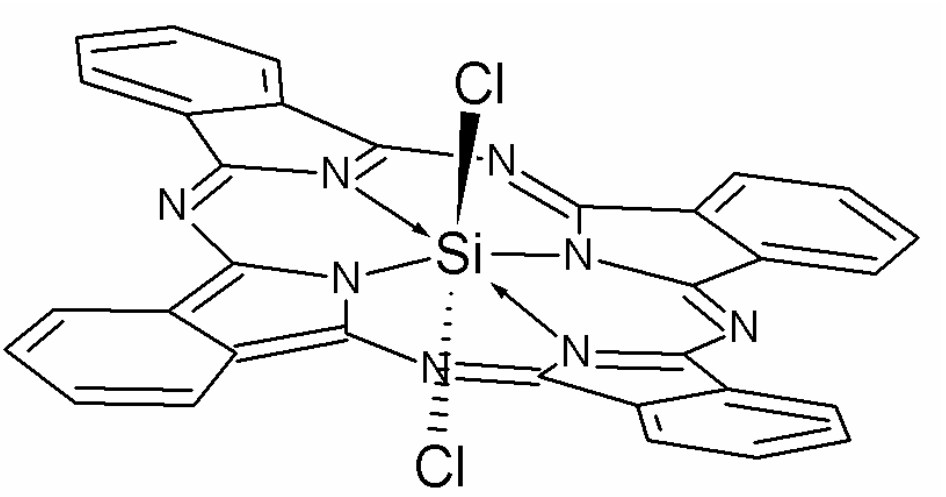
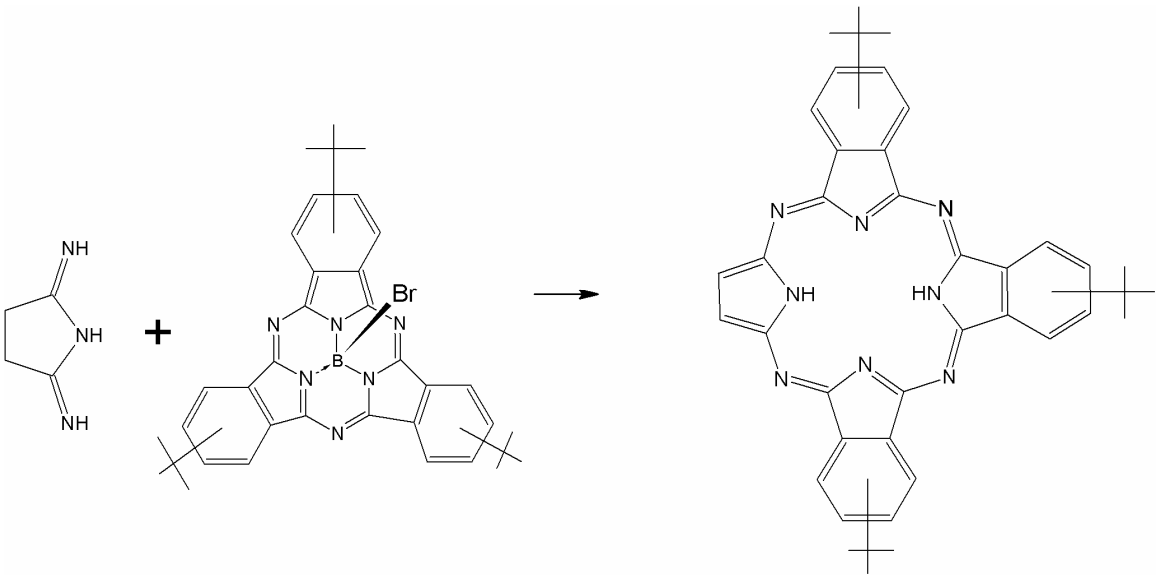


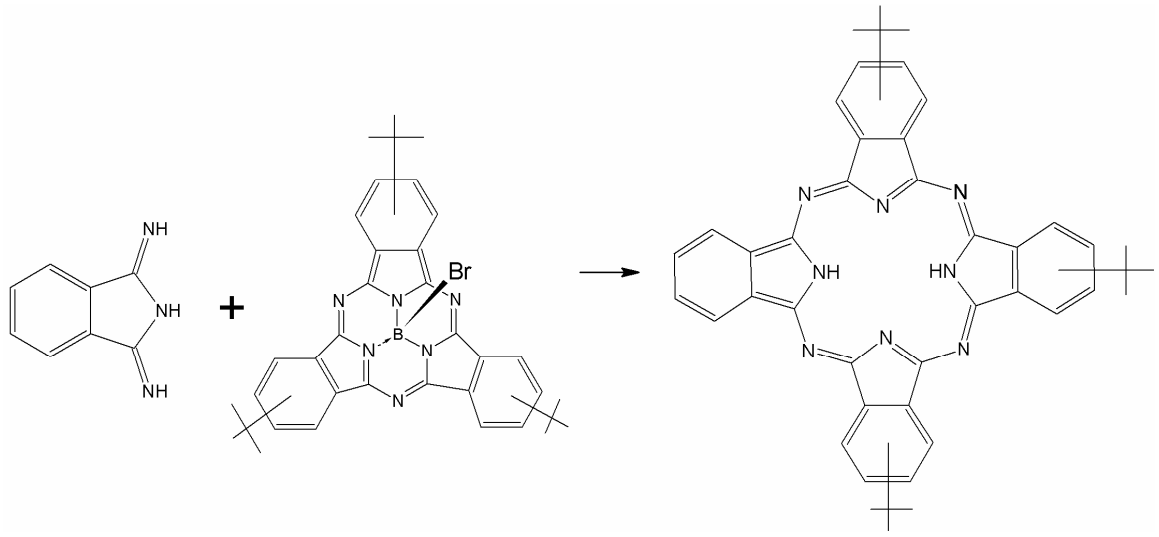
Figure 1.6 3-D representation of chloro[phthalocyaninato]silicon (IV).

As a class of compounds, subphthalocyanines remained relatively unexplored for a long time because of, in part, the troublesome processes required for their purification. When research on them finally began in the early 1990s, it was not for their own properties as much as it was for a study into the properties of the phthalocyanines, the larger homologues to the subphthalocyanines. It was found that asymmetrical phthalocyanines (hemiazaporphryins), which are difficult to synthesize otherwise, can be synthesized by a ring enlargement of subphthalocyanines.

In 1990, it was discovered that an asymmetrical phthalocyanine could be made by treating a subphthalocyanine with succinimide (Scheme 1.2) or a diisoiminoindoline analog (Scheme 1.3). Phthalocyanines were considered more stable than the subphthalocyanines, so it was believed the subphthalocyanines would be open to accepting an isoindole group and would become a monosubstituted form of the phthalocyanine to relieve ring strain. In the ring-enlargement reaction, the central metal atom and the axial ligand are lost from the ring structure and remain in the reaction solvent.[2, 5] The early investigations[6], which used general aromatic solvents such as toluene, benzene, or chloronapthalene, did not result in the synthesis of ring-enlarged phthalocyanines. Later, it was found that in mixed solvents containing DMSO and aromatic solvents, the ring enlargement did take place.[7] Since this discovery, many other investigations[6] into the ring enlargement of the subphthalocyanine to the substituted phthalocyanine have taken place.



Scheme 1.2 Asymmetrical preparation of phthalocyanine using succinimide.



Scheme 1.3 Asymmetrical preparation of phthalocyanine using diisoiminoindoline.

Phthalocyanines have been extensively studied and found to be applicable in a very wide range of areas. Likewise, the asymmetrical phthalocyanines also exhibit similar properties. The asymmetrical rings have certain advantages over

the symmetrical ones and have found applications in such fields as non-linear optics, thin-film formation, photovoltaics, and laser dyes.[8]

The resurgence of interest in subphthalocyanines was initiated by their importance as precursors for asymmetrical phthalocyanines; however, they are beginning to be used in other applications, for example, in the area of catalysis. Phthalocyanines hold promise as the next generation of electron-donor-based catalysts[9], though the research shows they can be used in catalytic reduction or oxidation processes. Phthalocyanine cobalt complexes have been used in the presence of oxygen in the catalytic oxidative polymerization of vinyl monomers to produce polyperoxides.[10] These polyperoxides are compounds of interest because of their physiochemical behavior, such as the ability to self-combust under the proper conditions, their use as initiators in base-catalyzed reactions, and the ability to self-pyrolyze, as well as their use for custom fuels and for coating and molding applications.[10] Phthalocyanine cobalt complexes are sought after because they are able to complete the polymerization reactions at lower temperatures than the conventional preparation method for polyperoxides.[10] This is important because the higher temperatures often lower the yield and limit the reaction as a result of the degradation of the product at raised temperatures. The hope is that this procedure will lead to the development of other polymerization processes for polymers that are temperature sensitive. There is also hope that synthetic oxygenated polymers can serve as a foundation for incorporating oxygen into biological polymers.[10]

Metal phthalocyanines are also effective catalysts for the reduction or oxidation of nitrogen compounds. For example, the synthesis of *p*-nitrobenzoic acid, an essential intermediate for many industrial applications, often uses toxic or hazardous oxidizing chemicals, such as nitric acid, potassium permanganate, sodium dichromate, sodium hypochlorite, and organic peroxides.[11] In addition to the health danger, the synthesis also produces large amounts of hazardous wastes. More environmentally friendly methods for the synthesis of *p*-nitrobenzoic acid are being sought. The current green method uses molecular oxygen, or ozone.[11] The drawback to using molecular oxygen is that it is difficult to activate under mild conditions. Another method uses bromide salts in solvents such as acetic acid.[11] This, too, has its problems, as it can lead to undesired side reactions. Cobalt phthalocyanine complexes with carboxyl groups attached to the phthalocyanine rings produce good yields of *p*-nitrobenzoic acid from *p*-nitrotoluene. This is a very significant step forward in the development of more environmentally friendly industrial processes.[11]

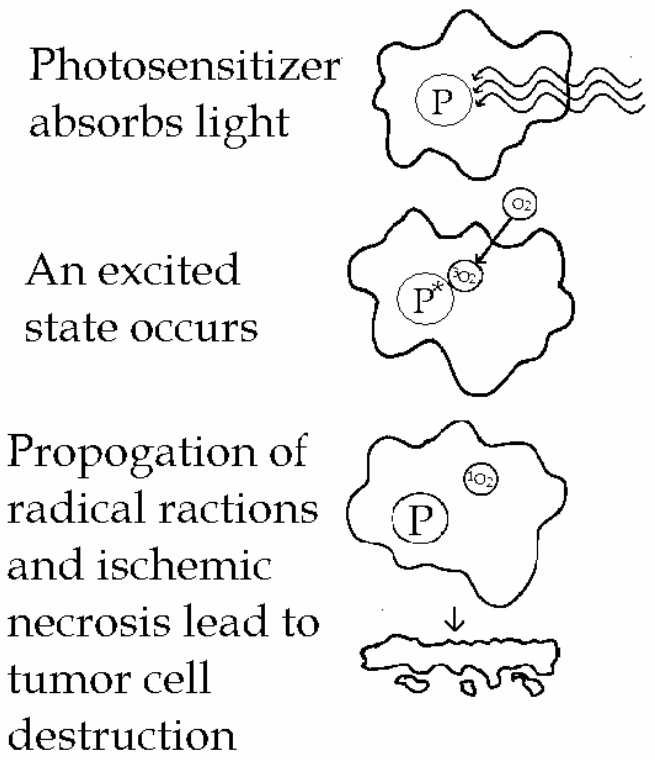
Reduction of nitrite and nitrate by dithionite in the presence of a cobalt phthalocyanine catalyst is of environmental and health importance as well. Nitrate, which is used in fertilizers, serves as a starting point for the nitrogen cycle in the environment. The nitrate is reduced to molecular nitrogen by action of bacteria in the soil. However, because the presence of nitrate or nitrite in drinking water is potentially harmful, methods to remove it are needed. It has been shown that cobalt phthalocyanine complexes are effective catalysts for the

reduction of nitrate and nitrite in the presence of dithionite. It was noted, surprisingly, that the reduction of the two substances gives two different reactions.[12] The reduction of nitrite yields ammonia, whereas the reduction of nitrate yields molecular nitrogen. The coordination, either nitrogen or oxygen, to the central metal atom determines the product.

Because of their aromatic-like character, the subphthalocyanines, similarly to phthalocyanines, often exhibit unusual electrical and optical properties unique to that class of compounds. These unusual properties have led to their use in non-linear optics and thin-film formation.[13]

Perhaps the most exciting and potentially life-saving use of the phthalocyanines' optical properties is in photodynamic tumor therapy for cancer.[14] In this treatment, the photosensitizer is allowed to accumulate in the tumor tissue. When irradiated with light, the photosensitizer absorbs energy and transfers that energy to diatomic oxygen. This transferred energy transforms the ground state (triplet oxygen) to an excited free radical state (singlet oxygen), which then destroys the surrounding cancerous tissue (Scheme 1.4). This therapy is very location specific, so the threat of harming healthy cells is minimal.[14] The phthalocyanines are highly regarded as one of the most desirable classes of compounds for this treatment because they are capable of transforming triplet oxygen to singlet oxygen with high quantum yields, and they have very large absorption coefficients. In order for the photosensitizer to be efficient at producing singlet oxygen, it must absorb strongly at the wavelength a laser

emits. For this reason, the development of new subphthalocyanines and phthalocyanines with wide absorption bands is desirable. In order to produce such compounds, new methods of synthesizing subphthalocyanines and symmetrical and asymmetrical phthalocyanines will need to be developed.[15] Phthalocyanines stabilized on gold nanoparticles increase their quantum yield of singlet oxygen. The free phthalocyanine has a singlet oxygen quantum yield of 0.45, whereas the nanoparticle-bound phthalocyanine has a singlet oxygen quantum yield of 0.65.[16] The higher quantum yields are due to an association of the phthalocyanine with the phase transfer agent used in their syntheses. Nanoparticles coated with phthalocyanines were also soluble in a wide range of polar solvents, which increases their effectiveness in biological media.[16]



Scheme 1.4 Photodynaminc tumor therapy process.

A problem that arises with the use of phthalocyanines in photodynamic therapy is their natural tendency to aggregate out of polar solvents. Methods are being developed to increase their solubility in polar solvents and to inhibit their tendency to aggregate out of polar solvents. Such methods to inhibit the aggregation include encapsulating the phthalocyanine in a biodegradable poly(sebacic anhydride) shell. These are then introduced into the tissue, where the shell degrades and the phthalocyanine is released.[17]

Another method being investigated to increase the solubility of phthalocyanines in biological media is the addition of hydrophilic axial ligands[18] to the phthalocyanine, as well as hydrophilic dendrimers to the phthalocyanine ring itself. Zinc phthalocyanine with multiple carboxylate groups were synthesized and evaluated in V79 hamster fibroblasts and human HEp2 cells.[19] These were taken in by the cells in good number and positioned themselves favorably within the cell. They also displayed other beneficial characteristics, such as low toxicity when not illuminated and sufficient toxicity when they are exposed to low levels of light.[19] One concern about photodynamic tumor therapy is that after the therapy is completed, the photosensitizer must be cleared from the body. This needs to be done in such a way that no more harm is done to the body and should be a fairly rapid process so that patients can be exposed to light after treatment.

Phthalocyanines are also being explored for their electronic properties, such as their usefulness in organic light-emitting diodes (OLEDs) and field effect

transistors (FETs). Organic-light emitting diodes have been developed sufficiently so that a broad range of devices with high efficiencies and reasonable lifetimes can be produced by vacuum deposition or polymerization.[20] Phthalocyanines are great candidates for OLEDs and FETs because of their inherent symmetry[21] and electroluminescent properties.[22] Uses of OLEDs include flat panel displays, smart cards, and radio-frequency identification tags.[23,24] Solid-state applications of phthalocyanines have been investigated because of their activity as a near-IR photoconductor.[25] Because of this, investigations into the spectra of certain phthalocyanines have been carried out to assess their compatibility and potential for these uses.[25]

Studies[26,27] have also been done to investigate their organization in thin films and how this affects their activity as organic semiconductors. Their physical arrangement on the surfaces has been shown to affect their ability to conduct electricity.[26] Solar cells and optoelectronics are also being sought after as applications of phthalocyanines. Chlorophyll, with a structure similar to that of the phthalocyanines, plays an essential role in photosynthesis. Using chlorophyll as inspiration, phthalocyanines are being looked into for the synthetic conversion of solar energy into chemical bonds.[27]

Phthalocyanines are organic p-type semiconductors. They have strong absorption in the visible region of the spectrum, high chemical stability, a high LUMO energy level, and high hole mobility. These properties make them ideal for photocopiers and organic solar cells.[28] However, it has been noted that in the

production of solar cells, ionized oxygen can accumulate and quench the singlet excited state at the TiO_2/ZnPc interface. This inhibits the photocurrents and thus limits the effectiveness of this type of solar cell. More research will need to be done to look at the possibility of efficient phthalocyanine-based organic solar cells.[28]

Phthalocyanines and their analogues exhibit nonlinear optical behavior. One requirement of nonlinear optics is absorption of light that is not linear and a change in frequency when illuminated.[29] There are various orders of nonlinear optics. Orders are based on how the frequency changes when the substance is illuminated. Subphthalocyanines that have second-order nonlinear optical properties have been studied in the solid state.[30] Phthalocyanines have also been investigated for chiral optical activity. The introduction of a chiral diol and chiral-branched alkyl side chains induced the formation of a stable, optically active dimer. The dimer was formed through the hydrogen bonding of the diols. This process can lead to the development of nanosize smart devices, which are made by the self-organizing process as a result of the chirality of the chains.[31]

In addition to photoluminescence, photolimiting properties of phthalocyanines have also been investigated. Because of the increase in the use of laser light and other high-intensity light sources, there is a growing need to protect sensitive optical instruments, including the human eye. Optical limiters are based on nonlinear optics, so phthalocyanines are an obvious choice. Optical limiting compounds absorb intense light of one frequency and then immediately

re-emit it over a broad range of frequencies that are much less dangerous. Phthalocyanines fit into these requirements very easily.[32]

Aside from cancer treatment, phthalocyanines can also be used in other forms of photodynamic therapy. Using the photosensitizer and laser light, one study showed how it was effective in killing 95%-100% of periodontal pathogens.[33]

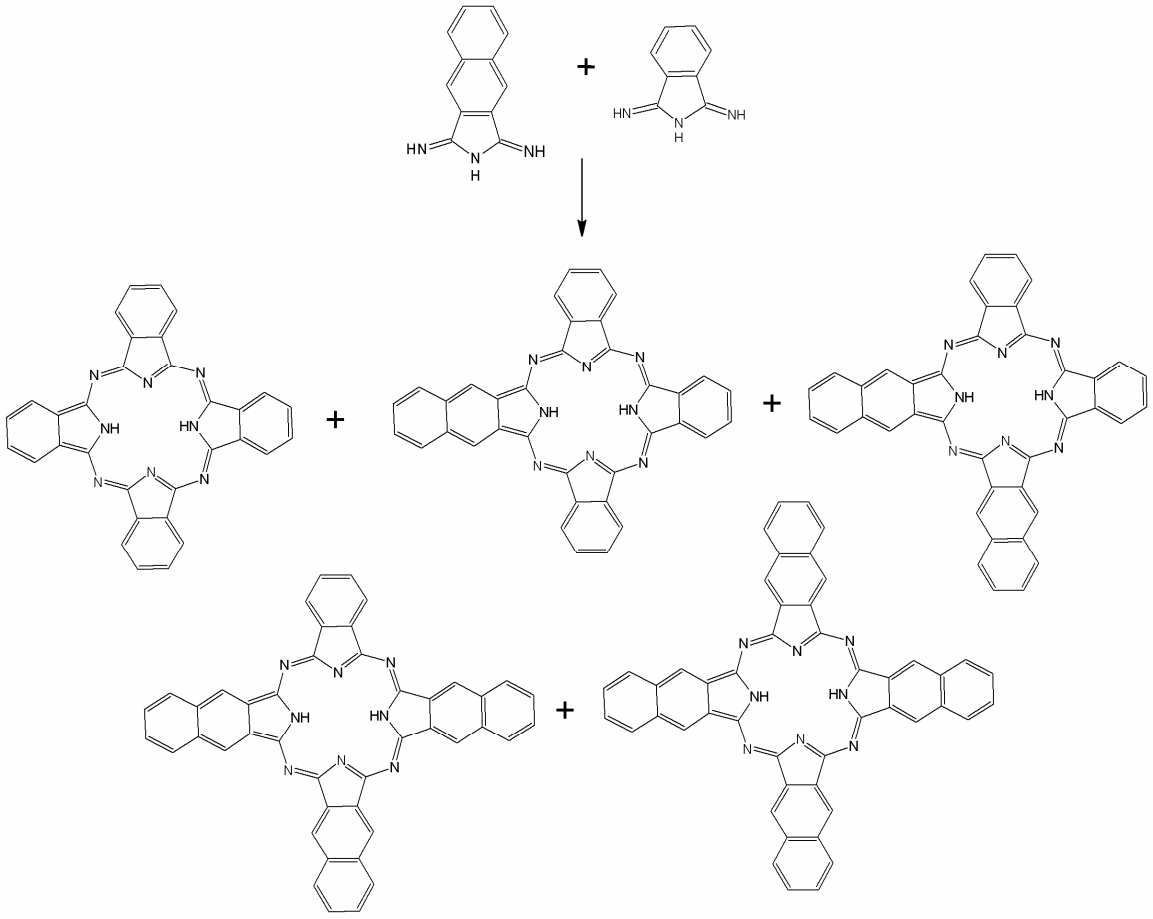
Phthalocyanines are also being used in bioanalytical investigations as labels for oligonucleotides. Near-IR fluorescence, which phthalocyanines offer, is attractive because there is no interference from the biological matrix, which there would be from visible light fluorescence. The phthalocyanine dyes were also successfully conjugated to oligonucleotides, which has the potential for use in near-IR based DNA diagnostic testing applications.[34]

Carbon nanotubes (CNTs) have a greatly diverse range of applications that come from their mechanical and electrical properties.[35,36] For some applications, having carbon nanotubes aligned proved to be more useful for evaluating their properties and easier for incorporating them into devices. Pyrolysis of various metal-containing phthalocyanines produced metal nanoparticles that are known to be effective catalysts for the growth of carbon nanotubes.[36] A combination of phthalocyanines and carbon nanotubes has been investigated in order to study their photoconductivity, and it was shown that the combination improved their photosensitivity of the composite material.[35]

It is quite apparent that the uses and applications for phthalocyanines go beyond simple chemistry. Phthalocyanines exhibit a very wide range of chemical applications, such as catalysts for polymerization reactions and reduction and oxidation reactions, as well as biochemical uses, such as dyes for oligonucleotides. Phthalocyanines have a medicinal use in photodynamic tumor therapy. Optically, phthalocyanines have a use as photolimiters because of their second-order, nonlinear optics. Mechanically, they can be used to produce metal nanoparticles that are then used as catalysts to produce aligned carbon nanotubes. Each one of these uses requires a specific phthalocyanine structured to fit a specific use. Therefore, as more applications for phthalocyanines are found, the need for more customized structures will increase as well. This will require the development of new methods of synthesis for phthalocyanines and phthalocyanine derivatives.

CHAPTER 2: REVIEW OF RELATED LITERATURE

In the synthesis of phthalocyanine from geometrically strained subphthalocyanine, the subphthalocyanine is reacted with a 1,3 diiminoisoindoline derivative. This forms a phthalocyanine that has three units from the original subphthalocyanine and one unit from the 1,3 diiminoisoindoline derivative.[37] This synthesis can yield symmetrical or asymmetrical phthalocyanines depending upon the 1,3 diiminoisoindoline group. The alternative to ring-enlargement reactions is to complete a statistical condensation reaction (Scheme 2.1) involving two different diiminoisoindolines or phthalonitriles, followed by tedious and repeated purification by chromatography. This, however, is not favored because the yields are not as high, it is not as selective, and purification is more complicated, as there are byproducts of the reaction.[38]



Scheme 2.1 Preparation of asymmetrical phthalocyanines using a statistical condensation.

Research[5,7,39-42] has shown that there are a few key components to successful ring-enlargement reactions: the nature of the peripheral substituents of the subphthalocyanine, the reactivity of the diiminoisoindoline derivative, the solvent, and the reaction temperature. In many of the ring-enlargement reactions, the reactions were carried out in a mixture of dimethylsulfoxide (DMSO) and 1-chloronaphthalene or dichlorobenzene (1:4 to 4:1) or in (dimethylamino)ethanol at 80-100 °C for 5-12 hours.

Table 1 shows the list of ring-substituted subphthalocyanines that have already been reacted to form phthalocyanines.[6] This is a rather limited list, so it is still rather early to draw conclusions about the effect of the ring substituents on the starting subphthalocyanine material. However, some research seems to show that strong electron-withdrawing groups, such as sulfonyl, allow the reaction to be carried out at lower temperature and can provide a higher selectivity for phthalocyanine formation.[39] There is some discussion about whether the axial substituent has any effect on the rate or the outcome of the reaction.[5,6]

Table 1. Subphthalocyanines That Have Been Investigated to Form Phthalocyanines via Ring Enlargement Reactions

Compound Number	R Peripheral Groups	X Axial Ligand
1	H	Cl
2	*tert*-butyl	Br
3	SC_6H_{13}	Cl
4	*tert*-butyl	Cl
5	NO_2	Cl
6	NO_2/*tert*-butyl	Cl
7	SO_2Cl	OH

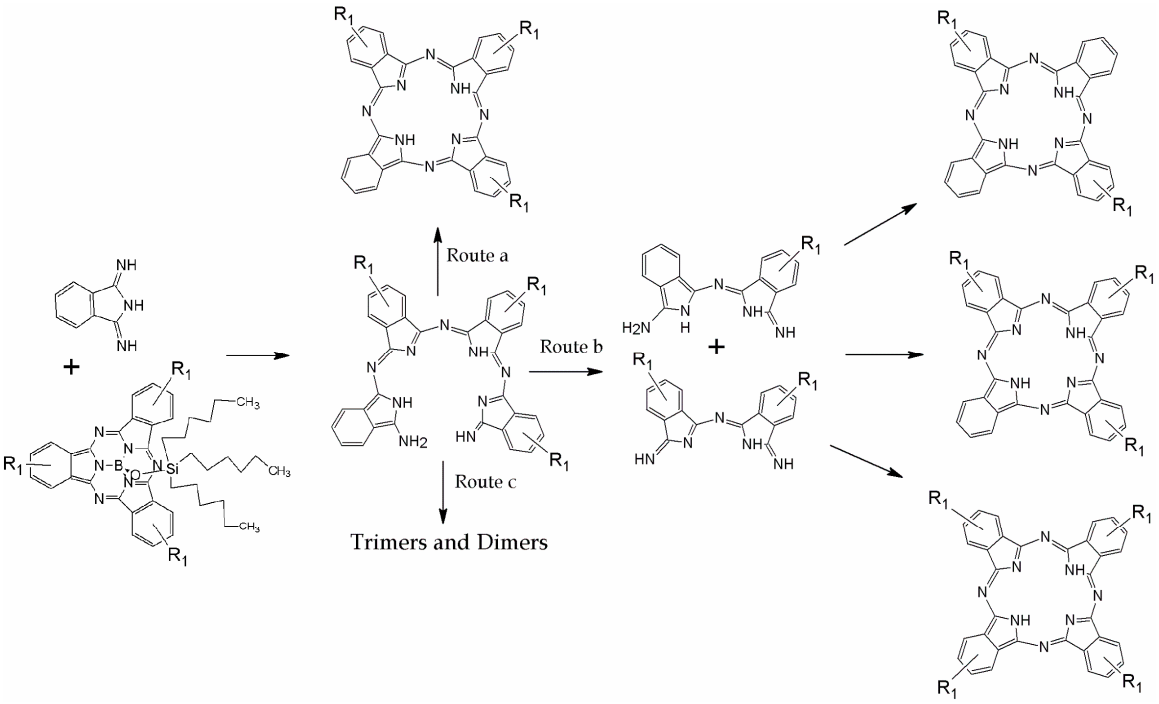
Perhaps the one part of these reactions that plays the greatest role is the 1,3 diiminoisoindoline derivative. Donor substituents on the diiminoisoindoline,

such as amino, amido bis(octyltriiodo), and *tert*-butyl, reduce its reactivity toward itself, thus reducing the possibility of self-condensation. These compounds are very selective, and only very small amounts of unwanted compounds are produced.[37] However, diiminoisoindoline derivatives with electron-withdrawing groups, such as nitro, sulfoxide, and sulfone, have a stronger tendency toward self-condensation because of their higher reactivity. Keeping the initial ratio of subphthalocyanine to diiminoisoindoline controlled to somewhere between 1:3 to 1:9 has been shown to minimize the effect of self-condensation.[40]

A major development in the ring-enlargement reaction was the discovery that transition-metal salts, such as zinc acetate[37], iron (II) sulfate[6], and nickel (II) chloride[40], increase the yield of asymmetrical phthalocyanines. Unfortunately, these salts also lead to higher yields of the other possible combinations of compounds. It was also demonstrated that in the presence of transition-metal salts, subphthalocyanines undergo spontaneous ring-enlargement reactions, leading to the symmetrical phthalocyanine.

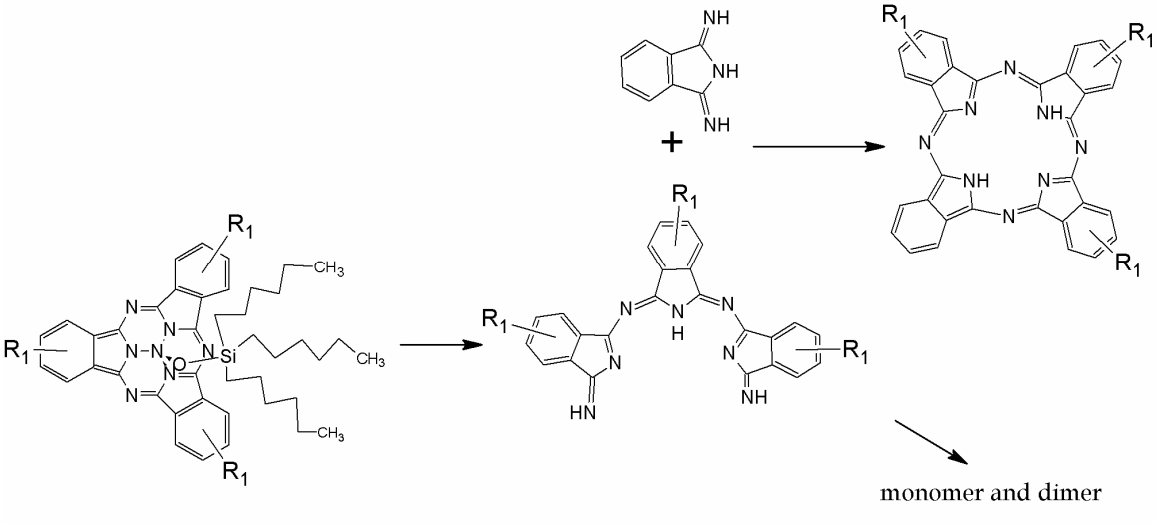
Three mechanistic pathways for ring enlargement have been proposed.[37] Pathway I: The reaction between the subphthalocyanine and the diiminoisoindole derivative (Scheme 2.2) produces an open, four-unit compound that could then react through three alternative methods: (a) the reaction may form the asymmetrical substituted phthalocyanine directly; (b) the subphthalocyanine and diiminoisoindole may be cleaved into smaller fragments,

either thermally or by attack of the solvent molecule to produce diiminoisoindoline or diiminoisoindoline dimmers; and (c) the open tetramer may be cleaved by another diiminoisoindoline molecule to produce dimers and trimers.



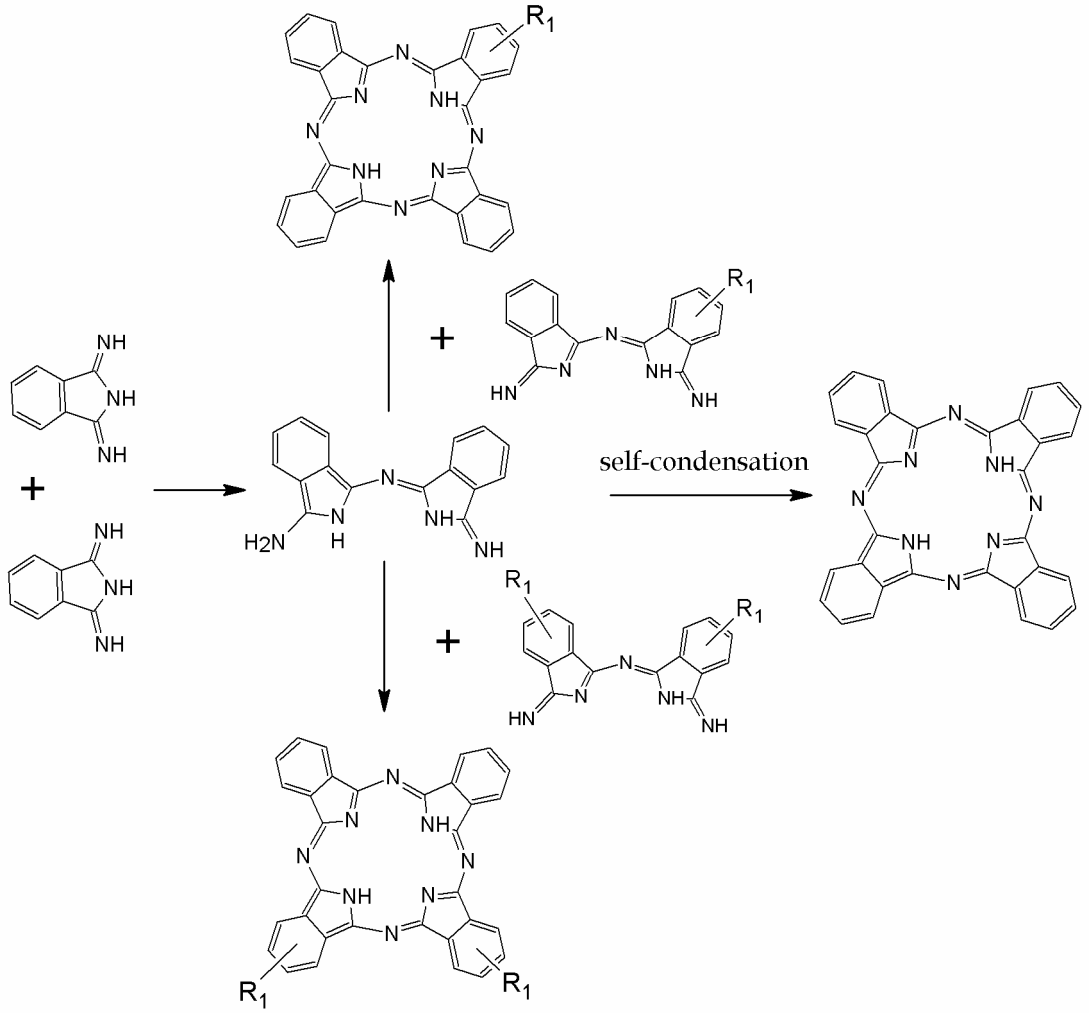
Scheme 2.2 Possible mechanisms for production of asymmetrical phthalocyanine products between diisoiminoindoline and subphthalocyanine. R_1 = H, Cl.

Pathway II: The subphthalocyanine macrocycle may be opened, which further reacts with the diiminoisoindoline (Scheme 2.3) or is broken into smaller units.



Scheme 2.3 Possible mechanisms for preparation of asymmetrical phthalocyanine via ring opening reaction with diisoiminoindoline. R_1 = H,Cl.

Pathway III: There is a self-condensation reaction of the diiminoisoindoline units to produce dimers (Scheme 2.4) that may then react with products from pathways I and II.



Scheme 2.4 Possible mechanism for the preparation of asymmetrical phthalocyanines via self-condensation of diisoiminoindoline. R_1 = H, Cl.

It is certainly possible that all of the intermediates from the three pathways may react further to produce a statistical mixture of all possible combinations of symmetrical and asymmetrical phthalocyanines. The effect that each pathway has on the overall reaction depends on the reaction conditions and the nature of the reactants.

Only the ring-opening synthesis reported by Kobayashi et al.[7] included a subnapthalocyanine. It involved a subnapthalocyanine that contained bromine as the axial ligand and hydrogen on the ring periphery.

CHAPTER 3: EXPERIMENTAL METHODS

Reagent

All reagents and solvents were used as obtained from the Aldrich Chemical company. The 80-200 mesh, neutral alumina that was used for chromatographic separations was used as obtained from Fisher Scientific.

Instrumentation

All ^{1}H NMR spectra were obtained with the use of a Brüker AC-250 spectrometer operating at 250 MHz,. The solvents used in obtaining the NMR spectra were deuterated benzene or chloroform. All UV-Vis spectra were obtained on a Perkin-Elmer λ 20 spectrophotometer with the Perkin-Elmer UV WinLab software package and quartz sample cells from Quaracell Products Inc. All UV-VIS spectra were obtained with the use of chloroform as the solvent. All IR spectra were obtained with the use of a Nicolet Impact 410 spectrophotometer with the Omnic E.S.P. 4.0 software package. The solvents used in the syntheses were toluene dried over CaH_2 and dichlorobenzene.

Synthesis of Trihexylsilanol:

In a 250-mL, round-bottom flask, 50 mL of diethylether, 5.0 mL of triethylamine, and 0.5 mL of water were combined, and the flask was set into an ice bath set upon a stir plate. A dropping funnel was charged with 10.0 mL (27.3

mmol) of chlorotrihexylsilane and 10 mL of diethyl ether. This was added to the contents of the flask over a period of one hour. A white precipitate was filtered off by gravity filtration, and the ether was evaporated off by a rotary evaporator. The remaining oil was chromatographed on Al_2O_3 (I) eluting with hexane. The solvent was evaporated, and the resulting oil had a mass of 5.93 g (71.2 %). ^1H NMR (250 MHz, $CDCl_3$): δ (ppm) = 0.34(t, 6H), 0.69(t, 9H), 1.06 (m, 24 H). IR (neat): $\nu(cm^{-1})$ = 3300 (br, OH).

Synthesis of Chloro[subphthalocyaninato]boron(III)

In a 100-mL, round-bottom flask, 1, 2 dichlorobenzene (55 mL) was dried by azeotropic distillation with the use of a Dean-Stark condenser and cooled to room temperature to drive off any water. 1,2 -dicyanobenzene (1.330 g, 10.38 mmol) and BCl_3 (25 mL, 1.0 M in heptane, 25 mmol) were added to the flask under N_2 gas. The heptane was distilled off from the side arm of the Dean-Stark condenser after heating to reflux. The reaction was then heated to reflux for another one and a half hours and then was cooled to room temperature. The flask was covered with aluminum foil during the reaction to protect it from the light. The solvent was evaporated off under rotary vacuum, and the remaining solid was placed in a soxhlet thimble. The crude product was extracted with methanol for four hours. After these washings were discarded, the solid was then extracted with chloroform for six hours. The solvent was evaporated, and the remaining solid was scraped from the round-bottom flask. The reaction

yielded 1.426 grams (89.18%). UV/Vis ($CHCl_3$): λ_{max}(nm), (ε, 1 x 10^4 $M^{-1}*cm^{-1}$) = 565.

Synthesis of Trihexylsiloxy[subphthalocyaninato]boron(III)

To a 100-mL, three-necked, round-bottom flask, 62 mL of dry toluene, 0.135g (5.86 mmol) of freshly cut sodium, and 1.30 mL of trihexylsilanol were added. The solution was heated to reflux to bring about the formation of the sodium salt of the silanol. The solution was cooled to room temperature, and 0.246 g (5.70 mmol) of neat chloro[subphthalocyaninato]boron(III) was added. The flask was covered with aluminum foil, brought back to reflux and, heated for one and a half hours. The solution and precipitate were transferred to a 100-mL, round-bottom flask, and the solvent was removed under vacuum. The solid was then scraped from the flask and dissolved in a minimal amount of toluene and chromatographed on Al_2O_3 (V). Toluene was used as the eluent to separate the unwanted products. The toluene from the desired collected fraction was removed under vacuum. The resulting oily, red liquid was chromatographed repeatedly on Al_2O_3 (I) with hexane and 5:1 (v:v) hexane:toluene as the eluents until a bronze solid was obtained (0.127 g, 32.0%). UV/Vis ($CHCl_3$): λ_{max}(nm), (ε, 1 x 10^4 $M^{-1}*cm^{-1}$) = 565.

Synthesis of Chloro[subnaphthalocyaninato]boron(III)

In an 500-mL, three-necked, round-bottom flask, 1,2 dichlorobenzene (100 mL) was dried by azeotropic distillation with the use of a Dean-Stark condenser and then cooled to room temperature. 2,3 Naphthalenedicarbonitrile (3.81 g, 21.4 mmol) and BCl_3 (70 mL, 1.0 M in heptane, 70 mmol) were added to the flask under N_2 gas. The reaction mixture was heated to reflux; the heptane was distilled off, and the mixture continued to heat for one and a half hours. The reaction flask was covered with aluminum foil to protect it from the light while the reaction was proceeding. The mixture was then transferred to a 250-mL, round-bottom flask, and the solvent was removed by rotary evaporation. Toluene was used as the eluent to chromatograph the crude product on Al_2O_3 (V). The solvent from the collected fraction was removed under vacuum, and the resulting solid was added to a thimble of a soxhlet extractor and extracted with chloroform for four hours. The solvent was removed under vacuum from the mixture, and the remaining blue solid weighed 1.666 grams (41.64%). UV/Vis ($CHCl_3$): λ_{max}(nm), (ε, 1 x 10^4 $M^{-1}*cm^{-1}$) = 650.

Synthesis of Trihexylsiloxy[subnaphthalocyaninato]boron(III)

In a 100-mL, three-necked, round-bottom flask, 70 mL of dry toluene, 0.34 g (14 mmol) of freshly cut sodium, and 5.2 mL (14 mmol) of trihexylsilanol were added. The solution was heated to reflux for 30 minutes to bring about the formation of the sodium salt of the silanol and then cooled to room temperature.

Any unreacted sodium was removed by hand from the mixture. To the solution 0.848 g (1.46 mmol) of chloro[subnaphthalocyaninato]boron(III) was added, and the flask was covered with aluminum foil to protect it from the light. The solution was heated to reflux for two hours. The mixture was cooled back to room temperature, and the solvent was removed under vacuum. Toluene was used as the eluent to chromatograph the solid on Al_2O_3 (I). The blue fraction was collected, and the solvent was evaporated by rotary evaporator. The resulting blue, oily liquid was mixed with methanol to dissolve the remaining silanol and precipitate the trihexylsiloxy[subnaphthalocyaninato]boron(III). The washings were centrifuged. The liquid was decanted off, and the solid was washed three more times with methanol and then centrifuged again. The remaining blue solid was collected and dried to yield 0.41 g (33%). UV/Vis ($CHCl_3$): λ_{max}(nm), (ε, 1 x 10^4 $M^{-1}*cm^{-1}$) = 651.

Symmetrical Ring-Enlargment Reaction of SubPc with Diiminoisoindoline

Trihexylsiloxy[subphthalocyaninato]boron(III) (0.13 g, 0.18 mmol) and 1,3 diiminoisoindoline (0.13 g, 0.76 mmol), 5.0 mL of dimethylsulfoxide, and 2.5 mL of toluene were added to a 25-mL, round-bottom flask. The flask was covered with aluminum foil and stirred at room temperature for 14 weeks. Thin-layer analysis showed no remaining starting material but did show the presence of a blue precipitate that did not move up the TLC plate. The solvents were evaporated by rotary evaporator. The remaining blue solid was rinsed with

methanol and placed in a centrifuge. The solid was rinsed with methanol three times. The washed solid was then collected and dried to yield 0.036 g (38%). UV/Vis ($CHCl_3$): λ_{max}(nm), (ε, 1 x 10^4 M^{-1}*cm^{-1}) = 656, 692. MS-HREI exact mass, m/z: calculated for $C_{32}H_{18}N_8(M)^+$ 514.1654; measured 514.1635.

Asymmetrical Ring-Enlargement Reaction of SubPc with Diiminobenz[f]isoindoline

Trihexylsiloxy[subphthalocyaninato]boron(III) (0.16 g, 0.23 mmol), 1,3 diiminobenz[f]isoindoline (0.16 g, 0.82 mmol), 5.0 mL of dimethylsulfoxide, and 2.5 mL of toluene were added to a 25-mL, round-bottom flask. The flask was covered with aluminum foil and stirred at room temperature for six weeks. Thin-layer analysis showed no remaining starting material. The solvents were evaporated by rotary evaporator. The remaining solid was rinsed with methanol and placed in a centrifuge. The solid was rinsed with methanol three times. The washed solid was then collected and dried to yield 0.017 g (13%). UV/Vis ($CHCl_3$): λ_{max}(nm), (ε, 1 x 10^4 M^{-1}*cm^{-1}) = 655, 689, 721. MS-HREI exact mass, m/z: calculated for $C_{36}H_{20}N_8(M)^+$ 564.1811; measured 564.1816.

Symmetrical Ring-Enlargement Reaction of SubNc with Diiminobenz[f]isoindoline

Trihexylsiloxy[subnaphthalocyaninato]boron(III) (0.036, 0.048 mmol), 1,3 diiminobenz[f]isoindoline (0.093 g, 0.48 mmol) 5.0 mL of dimethylsulfoxide, and

2.5 mL of toluene were added to a 25-mL, round-bottom flask. The flask was covered with aluminum foil and stirred at room temperature for six weeks. Thin-layer analysis showed no remaining starting material. The solvents were evaporated by rotary evaporator. The remaining solid was rinsed with methanol and placed in a centrifuge. The solid was rinsed with methanol three times. The washed solid was then collected and dried to yield 0.0020 g (7.0%). UV/Vis ($CHCl_3$): λ_{max}(nm), (ε, 1 x 10^4 $M^{-1}*cm^{-1}$) = 692, 721. MS-EI, m/z: calculated for $C_{48}H_{26}N_8(M)^+$ 714; measured 714.

Asymmetrical Ring-Enlargement Reaction of SubNc with Diiminoisoindoline

Trihexylsiloxy[subnaphthalocyaninato]boron(III) (0.041 g, 0.043 mmol), 1,3 diiminoisoindoline (0.069 g, 0.48 mmol), 5.0 mL of dimethylsulfoxide, and 2.5 mL of toluene were added to a 25 mL round bottom flask. The flask was covered with aluminum foil and stirred at room temperature for six weeks. Thin-layer analysis showed no remaining starting material. The solvents were evaporated by rotary evaporator. The remaining solid was rinsed with methanol and placed in a centrifuge. The solid was rinsed with methanol three times. The washed solid was then collected and dried to yield less than 1.0 mg (less than 3%). UV/Vis ($CHCl_3$): λ_{max}(nm), (ε, 1 x 10^4 $M^{-1}*cm^{-1}$) = 655, 691, 720.

Unsuccessful Condensation to Produce a Statistical Mixture of SubPc Through SubNc for Studying the Mechanism of the Ring-Opening Reaction

A. Preparation of Statisitical Condensation Products

In a 100-mL, three-necked flask, 1,2 dichlorobenzene (50 mL) was dried by azeotropic distillation with the use of a Dean-Stark condenser and then cooled to room temperature. 1,2 Dicyanobenzene (0.303 g, 2.34 mmol), 2,3 naphthalenedicarbonitrile (0.614 g, 3.44 mmol), and BCl_3 (5.0 mL 1.0 M in heptane, 5.0 mmol) was added to the flask under N_2 gas. This mixture was heated to reflux, and the heptane was distilled off the side arm of the Dean-Stark condenser. The reaction mixture was heated at reflux for two hours. The flask was then cooled to room temperature, and hexane was added to precipitate the solid, which was filtered under vacuum. The solid was rinsed with hexane twice more and dried. This solid was then added to a soxhlet thimble and extracted under methanol for three hours. The dark-brown washings were discarded, and the thimble was dried. The solid was then extracted with chloroform for three hours to collect purified product.

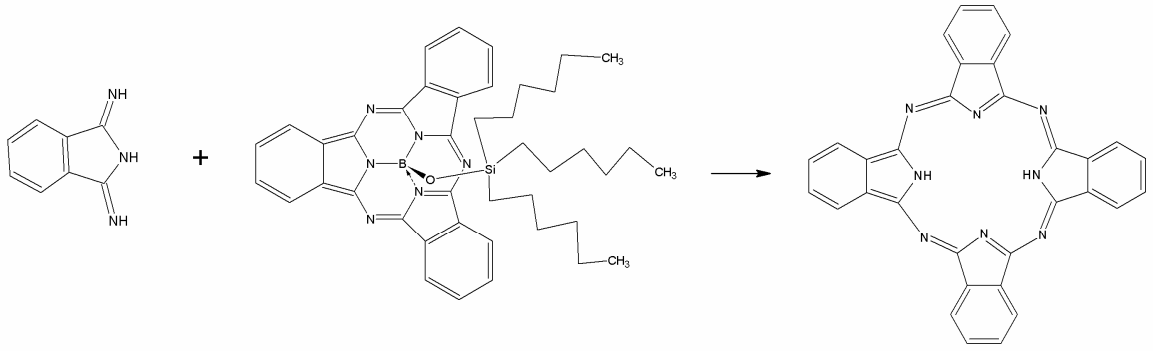
B. Capping Reaction of Statistical Reaction Products SubPc through SubNc

The trihexylsiloxy derivatives of the mixed cyclization products were prepared. In a 100-mL, round-bottom, three-necked flask, 50 mL of dried toluene, 0.137 g (5.96 mmol) of freshly cut sodium, and 1.3 mL (3.6 mmol) trihexylsilanol were added. The mixture was brought to reflux and heated for one hour. The reaction was cooled to room temperature, and excess

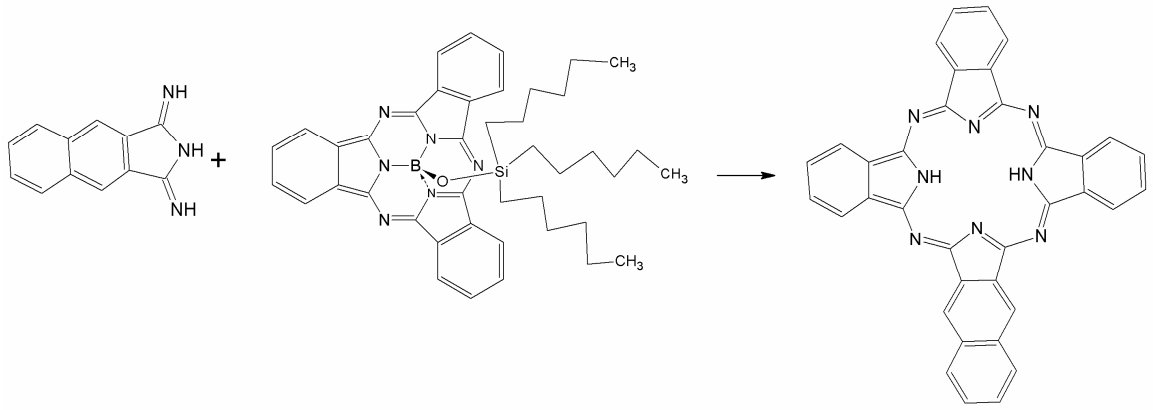
sodium was removed. Three hundred five thousandths grams of mixed cyclization product was added. The reaction mixture was heated to reflux for one and a half hours and then cooled to room temperature. The solvent was removed by rotary evaporator. The resulting oily liquid was chromatographed on Al_2O_3 (I) eluting in toluene. The solvent from the collected fraction was evaporated off by rotary evaporator. The oily liquid was then chromatographed repeatedly on Al_2O_3 (III) to separate fractions and separate oil. However, minimal product could be recovered after repeated chromatographies, and no further steps could be taken.

CHAPTER 4: RESULTS AND DISCUSSION

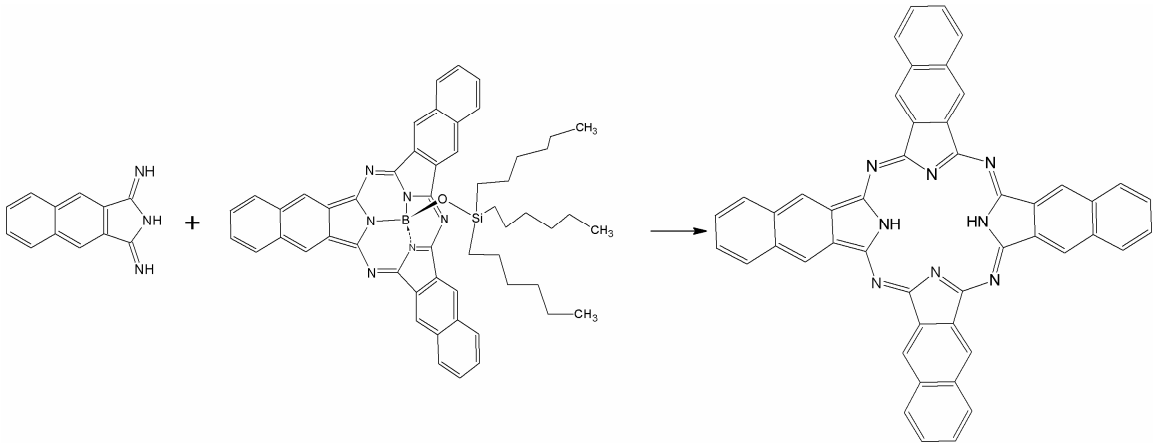
In order to obtain the toluene-soluble subphthalocyanine and subnaphthalocyanine, the chloro[SubPc]boron(III) and chloro[SubNc]boron(III) complexes had to be first synthesized and then reacted with the sodium salt of trihexylsilanol to produce to trihexylsiloxy[SubPc]boron(III) and trihexylsiloxy[SubNc]boron(III), respectively. This enhancement in the solubility in toluene and hexane proved invaluable in the isolation, purification, and characterization of trihexylsiloxy[SubPc]boron(III) and trihexylsiloxy[SubNc]boron(III) and made possible this new ring-opening synthesis. With the solubilizing group added to the SubPc and SubNc, the ring systems were then reacted with diiminoisoindoline or diiminobenz[f]isoindoline in order to produce symmetrical and asymmetrical phthalocyanine and naphthalocyanine ring systems (Schemes 4.1-4.4).



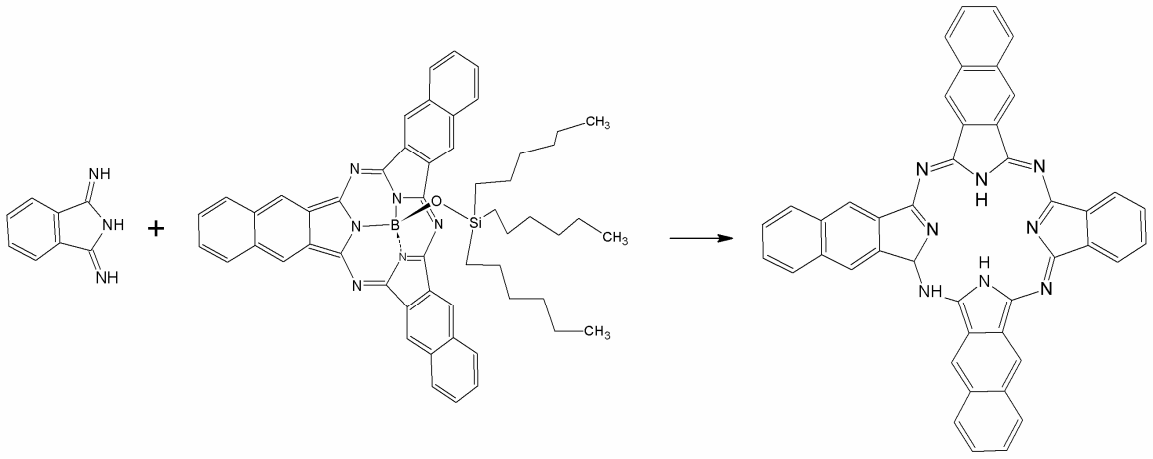
Scheme 4.1 Symmetrical phthalocyanine ring-opening reaction.



Scheme 4.2 Asymmetrical phthalocyanine ring-opening reaction.



Scheme 4.3 Symmetrical naphthalocyanine ring-opening reaction.



Scheme 4.4 Asymmetrical naphthalocyanine ring-opening reaction.

Characterization by UV-Vis spectroscopy and high-resolution electron-impact mass spectrometry indicates that at least three of the four reactions have succeeded. Future work, which would give additional support for the success of these reactions, would involve inserting a metal into the ring and adding substituents to impart solubility in common organic solvents would allow other methods of characterization, such as nuclear magnetic resonance (NMR) spectroscopy.

The UV-Vis spectrum obtained for each product shows at least two absorbance peaks that are within 70 nm of each other. This points toward metal-free phthalocyanines and naphthalocyanines, which exhibit this tendency. Metal-free phthalocyanines also tend to have absorbance peaks that are shifted higher from their normal absorbance peaks when containing a central metal atom.[43] The metal-free product is what is expected from the ring-opening reactions. The spectra also show absorbances in areas that suggest phthalocyanine and naphthalocyanine products.

The spectrum of the symmetrical ring-opened subphthalocyanine shows two absorbance peaks (Figure 4.1). One peak is at 656 nm and the other is at 692 nm. These maxima surround the accepted absorbance peak of copper phthalocyanine, which has an absorbance of 678 nm.[29] The dual absorbance peaks and their values give evidence of successful symmetrical ring expansion to the metal-free phthalocyanine. High-resolution mass spectroscopic analysis of the product indicates that the desired product was formed. The calculated mass

of the symmetrically ring-opened phthalocyanine is 514.1654 amu, and the measured value is 514.1634 amu.

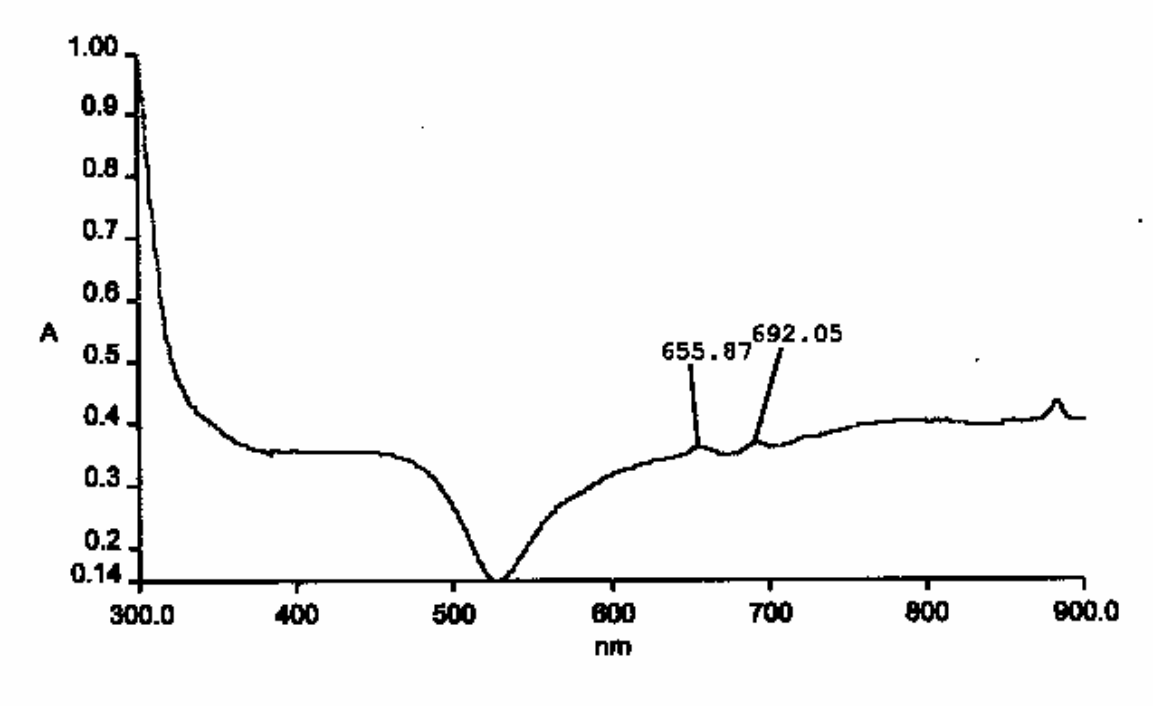


Figure 4.1 UV-Vis Spectrum for symmetrical ring-opening product of SubPc.

The spectrum of the asymmetrical subphthalocyanine ring-opening product, which should produce a ring structure with three phthalocyanine groups and one naphthalocyanine group (Figure 4.2), shows three absorbance peaks. There are absorbance peaks at 655 nm, 690 nm, and 721 nm. These peaks suggest some blend of phthalocyanine and naphthalocyanine. The dual 655-nm and 690-nm peaks again suggest a metal-free phthalocyanine; however, the 720-nm absorbance peak may suggest a naphthalocyanine piece. The typical

absorbance maximum for a full naphthalocyanine is 760 nm.[29] The absorbances were shifted to a lower wavelength, more toward the phthalocyanine absorbances because of the fact that it is metal free and as a result of some electronic influence from the phthalocyanine groups. High-resolution mass spectroscopic analysis of the product indicates that this was also the desired product. The calculated mass of the asymmetrically ring-opened phthalocyanine is 564.1811 amu, and the measured value is 564.1816 amu.

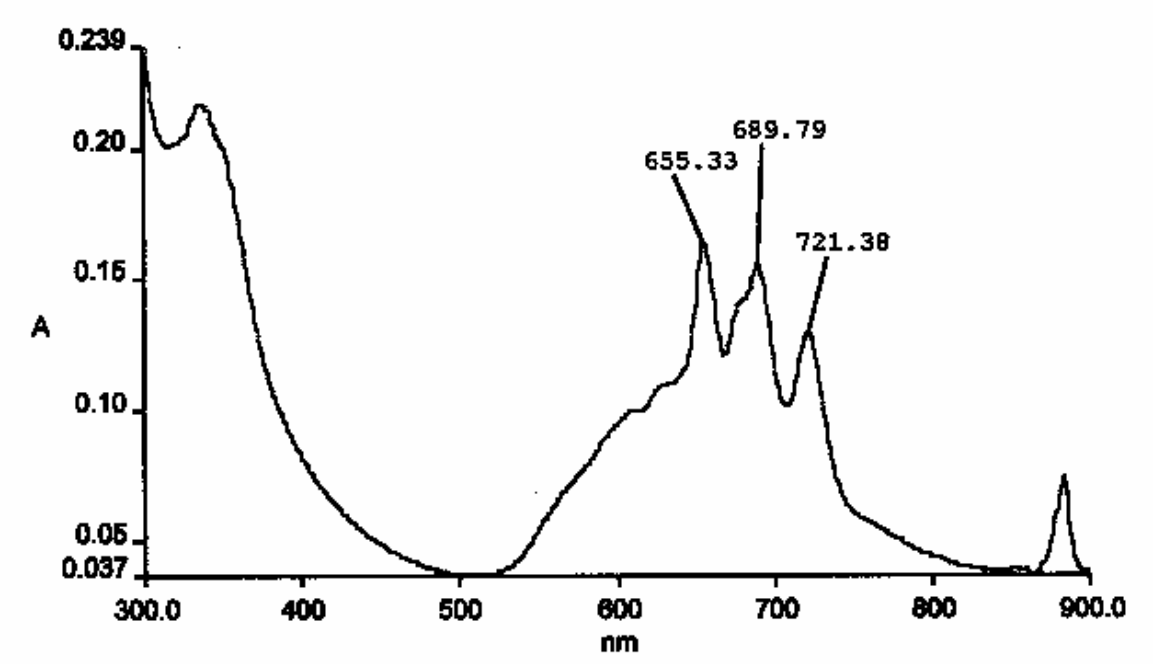


Figure 4.2 UV-Vis Spectrum for asymmetrical ring-opening product of SubPc.

The spectrum for the symmetrical subnaphthalocyanine ring-opening product, which should produce a symmetrical, metal-free naphthalocyanine ring (Figure 4.3), shows two absorbance peaks. The peaks have wavelengths of 692 nm and 721 nm. The typical absorbance-peak value for naphthalocyanine is 760

nm.[29] These two peaks are shifted to lower wavelengths, perhaps because of the lack of the central metal atom or chlorination of the ring. The appearance of two absorbance peaks points toward the existence of a metal-free naphthalocyanine. High-resolution mass spectroscopic analysis of the product could not be completed because of an extremely weak signal. However, the low-resolution spectrum included a measured mass peak at 714 amu, which agrees well with the calculated mass of 714.2280 amu for the desired product.

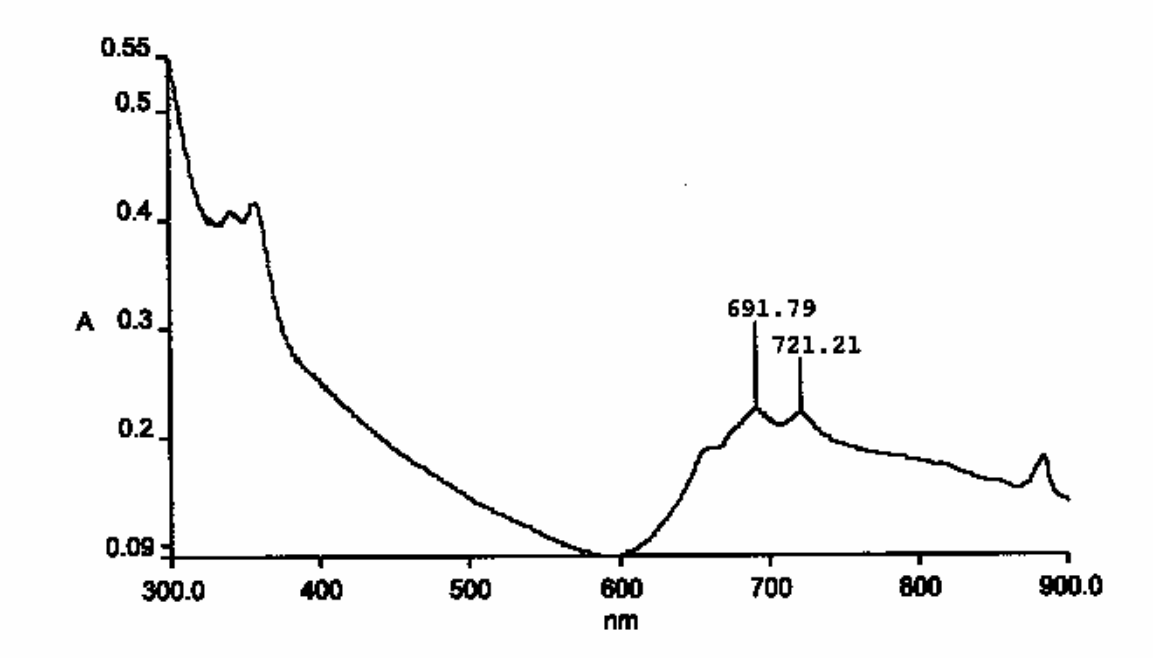


Figure 4.3 UV-Vis Spectrum for symmetrical ring-opening product of SubNc.

The spectrum for the asymmetrical subnaphthalocyanine ring-opening product, which should produce a ring structure with three naphthalocyanine ring units and one phthalocyanine ring unit (Figure 4.4), contains three peaks: 655 nm, 690 nm, and 720 nm. Again, this indicates that there are two different

ring systems present in the larger ring body. The fact that the absorbance maxima are nearly identical to those of the asymmetrical subphthalocyanine ring-opening product is surprising. However, the two are not identical in other regions, indicating that the compounds are not the same. High-resolution mass spectroscopic analysis of the product did not confirm the presence of the expected product. The expected mass peak was not found, and none of the mass peaks could be assigned to reasonable fragments of the expected product. It is unclear whether the sample was contaminated or whether the reaction did not succeed as desired.

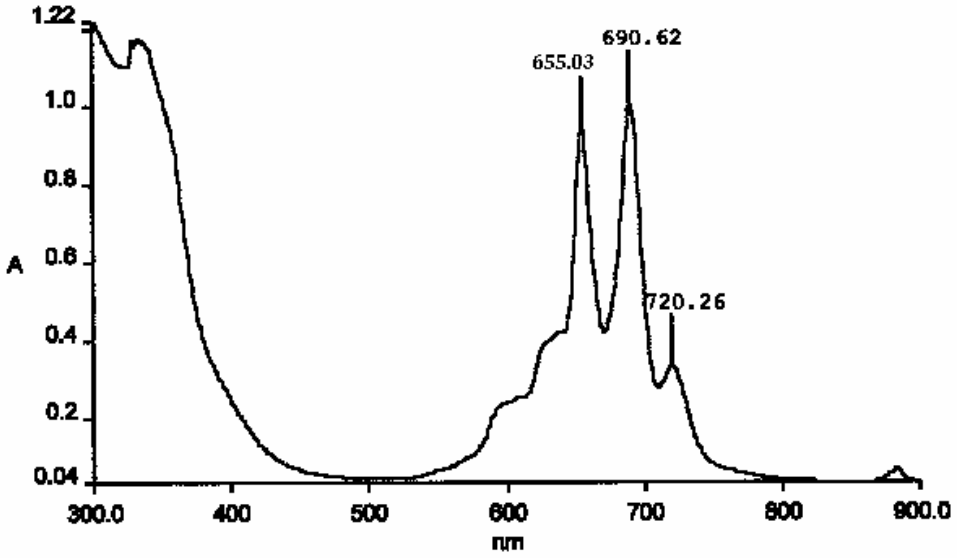


Figure 4.4 UV-Vis Spectrum for asymmetrical ring-opening product of SubNc.

This new ring-expansion pathway may open new methods for synthesizing asymmetrical phthalocyanines that are open to accepting central metal atoms. Future work could certainly look into optimizing the reaction

temperatures, solvents, and time. Also, future work could look into inserting different metal atoms into the empty center. Investigations into the synthesis and electronic properties, such as charge transfer, of asymmetric dimers may prove to be useful for applications covered earlier. The synthesis of asymmetrical rings may prove to be useful for many of the applications of phthalocyanines in which they must absorb light and use the energy to excite nearby particles, such as PDT. The more absorbance peaks, or the wider the peaks are, the more likely it is that a light source that emits light in that region will be found.

CHAPTER 5: CONCLUSIONS

Through this work, evidence has been found that yet another subphthalocyanine derivative can undergo a ring-enlargement reaction. In addition, the results show that subnaphthalocyanine is also able to undergo ring-opening reactions. What makes this reaction novel is its use of unique axial ligands on the central metal atom, the lack of intentional substitution of the main ring structure, and the synthesis of asymmetrical ring systems.

The discovery that the asymmetrical phthalocyanines and naphthalocyanines have three absorbance peaks in the region where two or even one absorbance peak would be expected is quite important. There is broad use of these compounds to capture light and use it to excite nearby molecules. By creating asymmetrical ring systems, it is possible to increase the number of effective and efficient light sources. Asymmetrical ring syntheses open new doors to customizing phthalocyanines. It is now possible to produce phthalocyanines that have their maximum absorbances at those frequencies emitted by lasers and at those frequencies best suited for the task at hand.

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