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NEW DIRECTIONS IN PHTHALOCYANINE PIGMENTS
(Center Director's Discretionary Fund Final Report No. 90-25)

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Science and Engineering Directorate

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NEW DIRECTIONS IN PHTHALOCYANINE PIGMENTS

INTRODUCTION

Phthalocyanines have been used as a pigment in coatings and related applications for many years. These pigments are some of the most stable organic pigments known. The phthalo blue and green pigments have been shown to be ultraviolet (UV) stable and thermally stable to over 400 °C. These phthalocyanines are both a semiconductor and photoconductor, exhibiting catalytic activity and photostabilization capability of polymers. Many metal-free and metallic phthalocyanine derivatives have been prepared. Development of new classes of phthalocyanine pigment could be used as coatings on NASA spacecraft material such as glass to decrease the optical degradation from UV light, on the outside of the space station modules for UV protection, and as a coating on solar cells to increase lifetime and efficiency.

OBJECTIVE

The proposed research targeted the synthesis of phthalocyanines containing an aromatic bridge between two phthalocyanine rings. The goal was to synthesize pigments which would protect plastic when exposed to the photodegradation effects of the Sun in space. The stability and extended conjugation of the phthalocyanines offer a unique opportunity for energy absorption and numerous radiative and nonradiative energy loss mechanisms. The investigation was conducted in four major tasks:

1. Investigation of the synthesis of new phthalocyanines
2. Characterization of the new phthalocyanines synthesized
3. Utilization of quantum mechanics to evaluate the structural relationships with possible properties and synthetic approaches
4. Investigation of the properties of newly synthesized phthalocyanines with emphasis on UV protection of plastic and coating.

RESULTS AND DISCUSSION

The first phthalocyanine synthesis attempted was that of compound 3 which was to be prepared according to the method shown in figure 1. The initial attempts to synthesize the bisphthalocyanine using perylene-3,4:9,10-tetracarboxylic acid dianhydride as the core resulted in only the formation of an amide-type product, compound 4. Several variations in the synthetic approach yielded only compound 4.

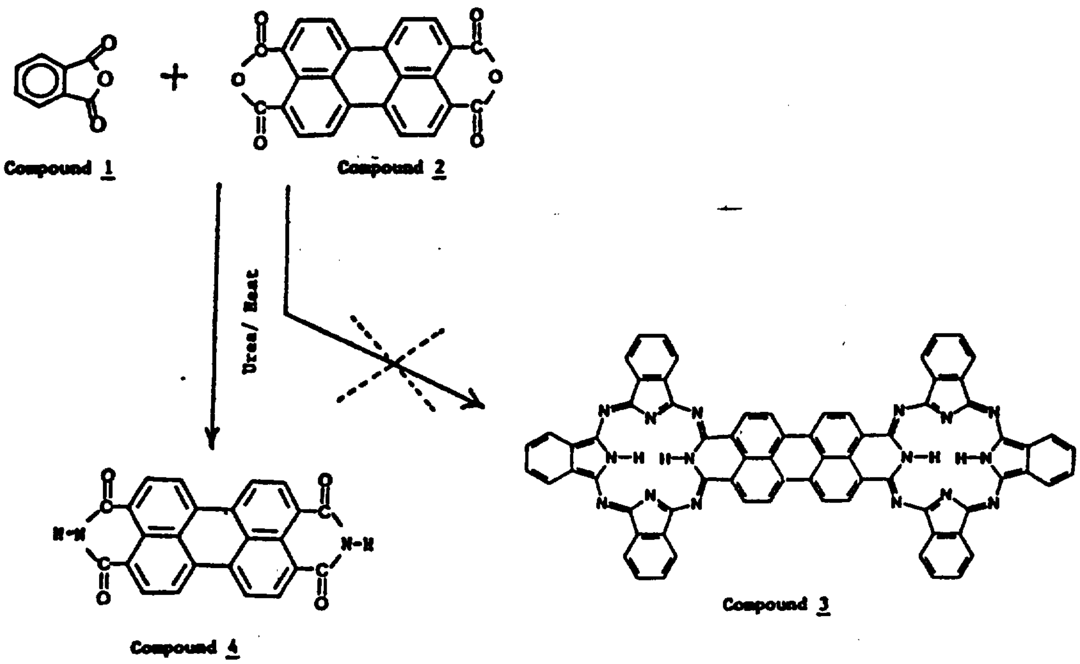
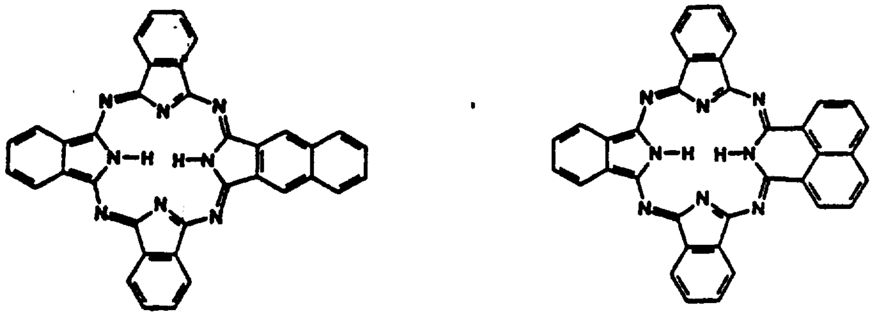


Figure 1. Preparation method of compound 3.

Initial theories included the possibility of too much steric hindrance near the perylene core or that the pi system is unstable.

The stability of the aromatic ring system of compound 3 was in question, therefore, the AMPAC computer program was employed to compare the heat of formation and the ionization potential of the two model compounds shown in figure 2. Here, a naphthalene ring is incorporated such that one is in a normal five-membered ring, compound 5, while compound 6 has the same six-membered ring that perylene would have. Compounds similar to compound 5 have been synthesized and are stable. Compound 6, however, has to date never been synthesized. Based upon the very similar ionization potential (IP) and heats of formation (HF), they both should be stable and able to be synthesized.



Compound 5	Compound 6
H.F. = 274.11 Kcal	H.F. = 273.99 Kcal
I.P. = 6.995 EV	I.P. = 6.934 EV

Figure 2. Models of compounds 5 and 6.

Phthalic anhydride and naphthalene 1,8-dicarboxylic acid were reacted with urea in an attempt to produce compound 6. The reaction produced a dark-colored material contaminated with compound 7, phthalo blue. Thus, no new phthalocyanine was produced in a detectable amount. The reaction was apparently somewhat inhibitory to the formation of compound 7 also, since its yield was less than expected.

In an effort to understand the absence of compound 6 in the reaction, AMPAC was used to evaluate the intermediates which are involved in the formation of phthalocyanines. The application of modify neglect of differential overlap (MNDO) calculations to compound 5 and 6 are given below.

The following calculation was on a model compound using a single naphthalene unit as a prototype for the perylene structure. Further analysis will require careful examination of the bond order matrix.

Compound 6 - mono-1,8-naphthalene phthalocyanine $C_{36}H_{20}N_8$

```
    HEAT OF FORMATION      = 273.994899 KCAL
    GRADIENT NORM          = 0.428630
    DIPOLE                 = 8.50378 DEBYE
    NO. OF FILLED LEVELS   = 102
    IONIZATION POTENTIAL   = 6.933565 EV
    MOLECULAR WEIGHT       = 564.608
    SCF CALCULATIONS       = 1,129
    COMPUTATION TIME       = 9,683.07 SECONDS
GRADIENTS GNORM = 0.1 T = 18,000 BONDS XYZ
```

The following structure is similar to the above molecule except that the naphthalene ring is in the conventional orientation.

Compound 5 -mono-2,3-naphthalene phthalocyanine $C_{36}H_{20}N_8$

```
    HEAT OF FORMATION      = 274.109605 KCAL
    GRADIENT NORM          = 0.516983
    DIPOLE                 = 7.72256 DEBYE
    NO. OF FILLED LEVELS   = 102
    IONIZATION POTENTIAL   = 6.994719 EV
    MOLECULAR WEIGHT       = 564.608
    SCF CALCULATIONS       = 814
    COMPUTATION TIME       = 7,214.91 SECONDS
GRADIENTS GNORM = 0.1 T = 72,000 BONDS DENSITY XYZ
PHTHALOCYNINE Naphthalene in the normal mode.
```

The synthesis of phthalocyanines has been investigated by numerous research groups. The key intermediate which has been found to be critical in phthalocyanine formation is compound 8. It can be formed from phthalic anhydride (compound 1) reacting with urea or 1,2-dicyanobenzene (compound 7) reacting with ammonia. The best method for preparation is through 1,2-dicyanobenzene. The intermediate compound 8 can have a tautomer compound 9. Compound 9 has never been observed, which implies that compound 8 is more stable than compound 9. Some researchers believed that the observed spectra is really an average of the two tautomers, and that the tautomerism is very rapid. Their stability through AMPAC calculations have been investigated. In addition, the two tautomers for the naphthalene case, compounds 10 and 11, have also been calculated.

Figure 3 is the result of optimization for two possible phthalocyanine intermediates, compounds 8 and 9 and compounds 10 and 11, by MNDO to GNORM (normal gradient) = 0.5 level. The structural assignment was set by first using SYBYL to define the coordinate input to AMPAC and then to optimize by AMPAC. These two structures and their tautomers are key intermediates in the synthetic process. It should be noted that compound 8 is of lower energy than compound 9 by 3.018 Kcal. However, compound 10 is less stable than compound 11 by 1.234 Kcal. This would imply that their chemistry may also be different. The synthetic attempts using the precursor to compound 10, i.e., the anhydride, did not produce phthalocyanine, but the precursor to compound 8 did. To determine if this energy difference, which favored the alternate tautomer, was generally applicable for all 1,9-naphthalene systems, several different mono and disubstituted versions of compounds 10 and 11 were evaluated using AMPAC.

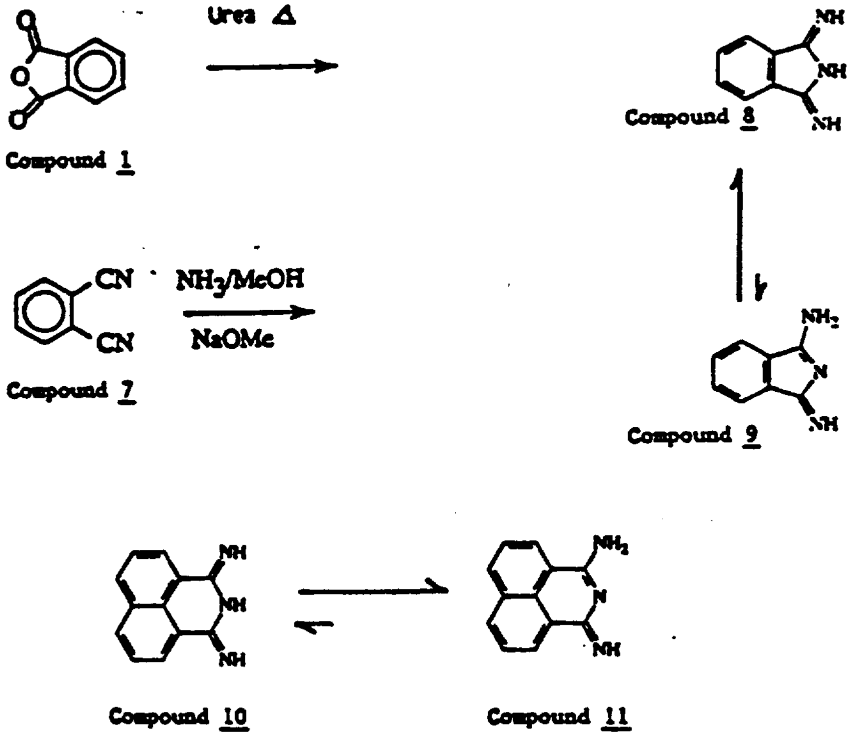


Figure 3. Two possible phthalocyanine intermediates of compounds 8 and 9 and compounds 10 and 11.

AMPAC has been used to evaluate various substituted naphthalene imide bisimines as to the stability of it versus its tautomer. The theory of the intermediate being the cause for the inability of these type compounds to form phthalocyanine-like systems may indeed be true. Using a substituted naphthalene system, a synthetic advantage might be gained. The object is to find the best group or groups which destabilize the tautomer relative to the parent bisimine. If the theory is correct, the new naphthalene system should form the phthalocyanine. These calculations have produced very interesting results, as can be seen from figures 4 and 5. For this report, only a subset of the data AMPAC was chosen. The values of heat of formation and ionization potential are shown for each structure. A valid level of optimization for each structure has been reached. The results given are for MNDO calculations at GNORM = 0.1. The confidence level for this type of calculation for similar structures is quite high. The substituents examined here are methoxy, fluorine, and hydrogen.

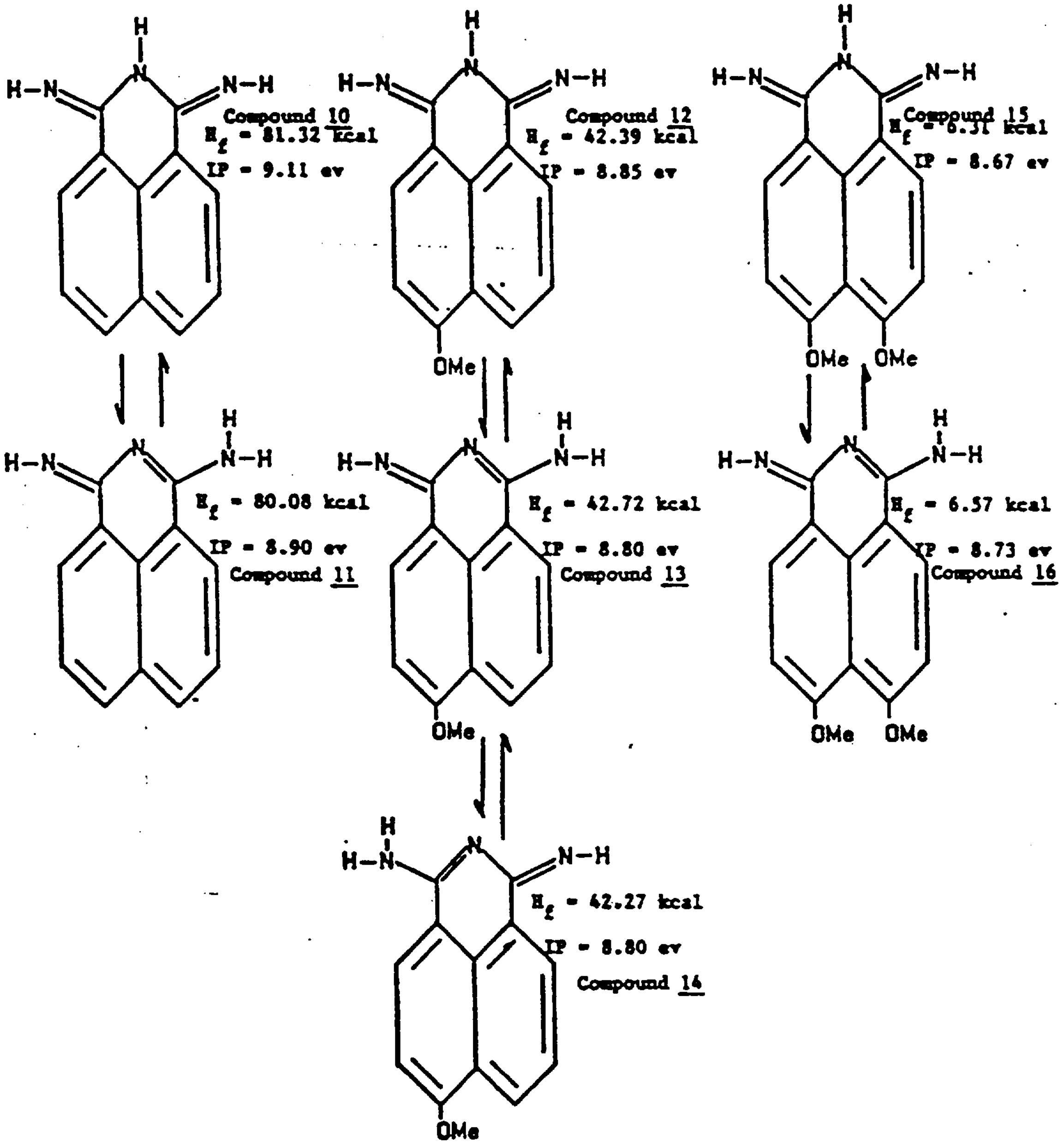


Figure 4. Structure and data for methoxy substituted naphthalene imide bisimines as to the stability of it versus its tautomer.

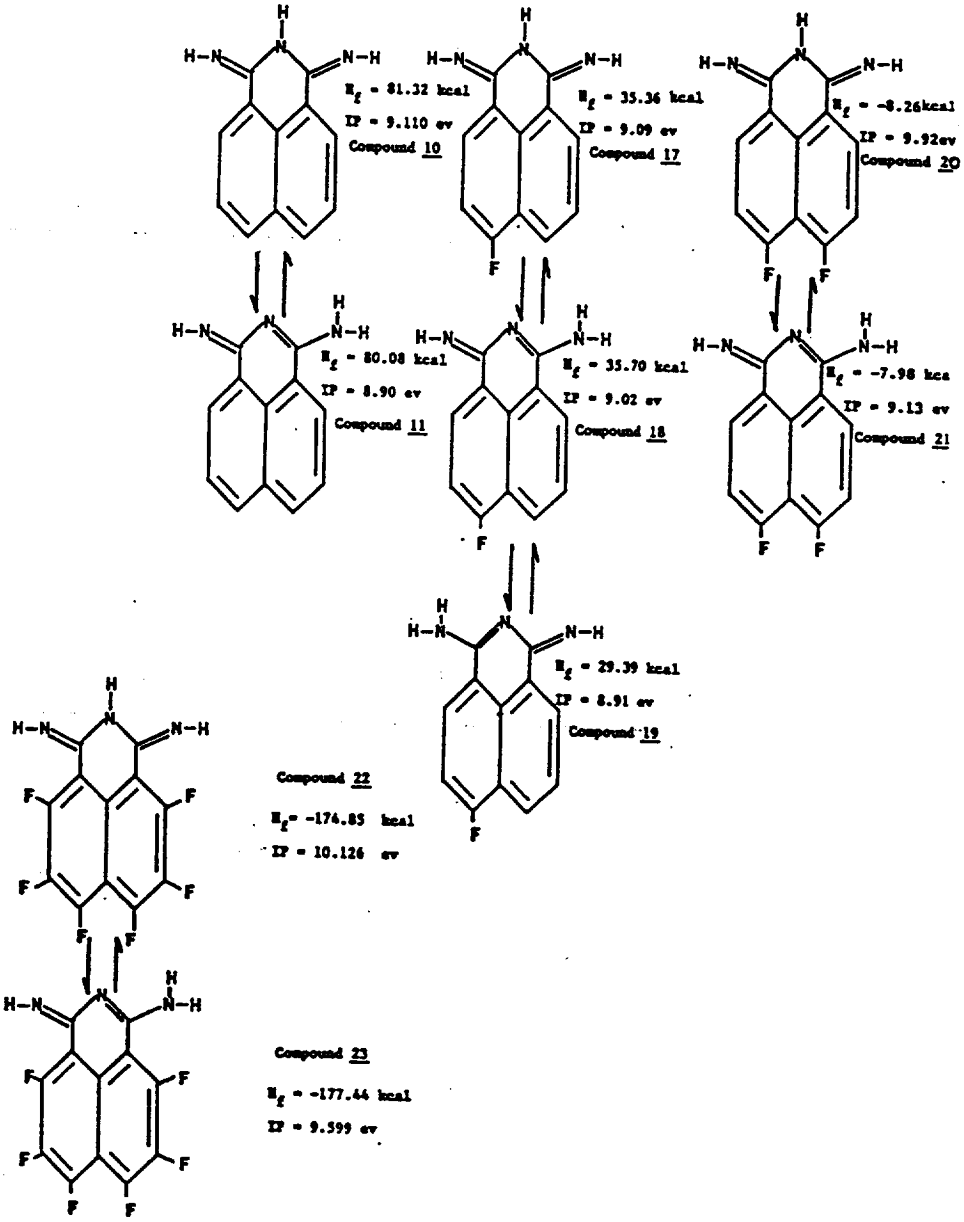


Figure 5. Structure and data for fluorine and hydrogen substituted naphthalene imide bisimines as to the stability of it versus its tautomer.

As can be seen in the heats of formation, H_f, and the ionization potential, IP, given on the following pages for compounds 12 to 23, only the difloro-substituted structure produces a heat of formation for the bisimine which is lower in energy than the other tautomers. The lower energy finding is a critical piece of information in this synthetic design. It implies that only the difloro system should produce the phthalocyanine if the bisimine is the key intermediate. Ways to approach the synthesis of the difloro compound for future work are investigated, however, this synthesis may prove to be a significant undertaking.

To test if compound 10 or compound 11 is the most stable, its synthesis via the commercially available napthalimide, compound 24, was attempted as shown in figure 6. Numerous attempts were made with only starting material being isolated from the first step. This synthetic pathway has been used successfully to convert phthalimide to 1,2-dicyanobenzene, compound 7.

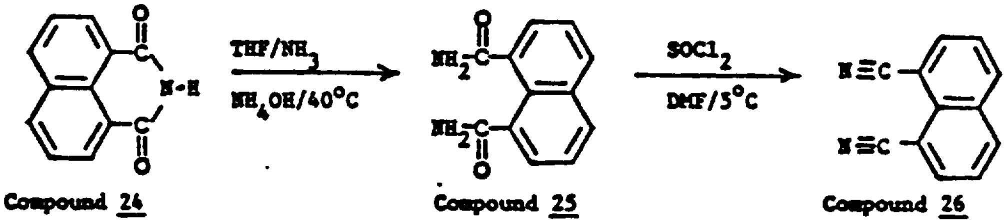


Figure 6. The scheme for synthesis of 1,8 dicyanonaphthalene.

The question of why this reaction does not work with the naphthalene analog was addressed again with AMPAC. The AMPAC program was used to determine the differences between the starting materials and products, as compared to phthaliminde, compound 27. It can readily be seen from the data shown below that the phthalimide should proceed, but that of naphthalimide should not.

The above finding may imply that the formation of the intermediate may be as problematic as the two tautomers, compounds 10 and 11. 1,8-dicyanonaphthalene has been synthesized through the Sandmeyer reaction (fig. 7). This method involves converting 1,8-diaminonaphthalene to the bidiazonium salt and reaction with copper bromide and hydrogen bromide to give 1,8-dibromonaphthalene, compound 31. The dibromide is then purified and reacted with copper cyanide in N,N-dimethylformamide, which produces 1,8-dicyanonaphthalene, compound 26. The overall yield for this process is extremely low, and the process is laborious. This process was, however, used successfully to produce the 1,8-dicyanonaphthalene.

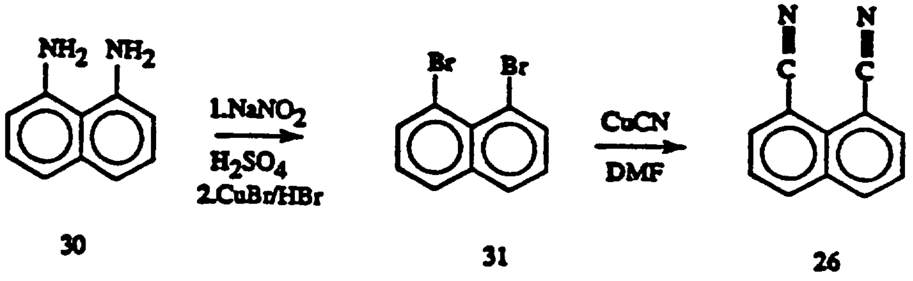
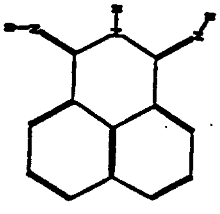


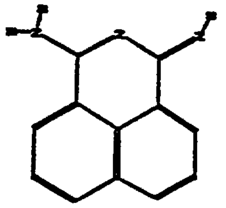
Figure 7. Synthesized 1,8 dicyanonaphthalene through the Sandmeyer reaction.

The conversion of 1,8-dicyanonaphthalene, compound 26, to the key intermediate, compound 10/11, was accomplished by bubbling ammonia through a methanol/1,2-dimethoxyethane solution of compound 26 with a catalytic amount of sodium. The reaction proceeded rapidly and produced a clean product with only minor impurities. The product was chromatographed on alumina to produce a pure



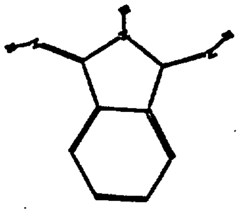
Compound 10

MNDO RHF: ΔH = 79.493 KCAL
IP = 8.861 EV
MNDO UHF: ΔH = 71. 523 KCAL
IP = 9.283 EV
AM1 UHF : ΔH = 91.224 KCAL
IP = 9.110EV
AM1 RHF : ΔH = 93.575 KCAL
IP = 8.881 EV



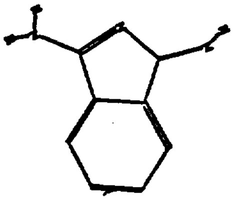
Compound 11

ΔH = 74.184 KCAL
IP = 8.782 EV
ΔH = 64.123 KCAL
IP = 9.066 EV
ΔH = 88.316 KCAL
IP = 8.758 EV
ΔH = 92.353 KCAL
IP = 8.745 EV



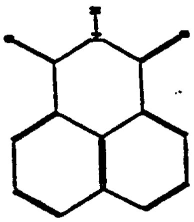
Compound 8

MNDO RHF : ΔH = 65.901 KCAL
IP = 9.622 EV
MNDO UHF : ΔH = 63.267 KCAL
IP = 9.743 EV
AM1 UHF : ΔH = 85.752 KCAL
IP = 9.590 EV
AM1 RHF : ΔH = 85.923 KCAL
IP = 9.565 EV



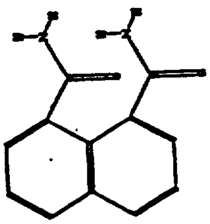
Compound 9

ΔH = 69.025 KCAL
IP = 9.682 EV
ΔH = 66.586 KCAL
IP = 9.788 EV
ΔH = 90.744 KCAL
IP = 9.529 EV
ΔH = 90.744
IP = 9.529 EV



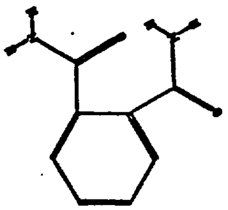
Compound 24

ΔH = -34.765 KCAL
IP = 9.355 EV
ΔH = -41.429 KCAL
IP = 9.700 EV
ΔH = -24.981 KCAL
IP = 9.626 EV
ΔH = -23.600 KCAL
IP = 9.484 EV



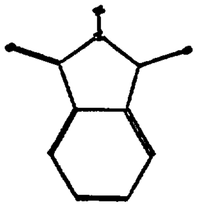
Compound 25

MNDO RHF :ΔH = -25.512 KCAL
IP = 9.134 EV
MNDO UHF :ΔH = -33.326 KCAL
IP = 9.542 EV
AM1 UHF : ΔH = -27.298 KCAL
IP = 9.383 EV
AM1 RHF : ΔH = -25.314 KCAL
IP = 9.172 EV



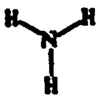
Compound 27

MNDO RHF : ΔH = -49.674 KCAL
IP = 10.069 EV
MNDO UHF : ΔH = -51.705 KCAL
IP = 10.335 EV
AM1 UHF : ΔH = -54.025 KCAL
IP = 10.207 EV
AM1 RHF : ΔH = -54.007 KCAL
IP = 10.198 EV



Compound 28

ΔH = -48.817 KCAL
IP = 10.271 EV
ΔH = -48.657 KCAL
IP = 10.497 EV
ΔH = -26.086 KCAL
IP = 10.494 EV
ΔH = -26.085 KCAL
IP = 10.480 EV



Compound 29

MNDO RHF : ΔH = -6.051 KCAL
IP = 11.192 EV
MNDO UHF : ΔH = -6.051 KCAL
IP = 11.192 EV
AM1 UHF : ΔH = -7.283 KCAL
IP = 10.421 EV
AM1 RHF : ΔH = -7.283 KCAL
IP = 10.421 EV

Figure 8. AMPAC calculation for various tautomers.

product, compound 11. The AMPAC calculations (fig. 8) were borne out in the prediction that compound 11 would predominate over compound 10. It should be noted that not only is this a significant finding in itself, but the question of whether the tautomerism is rapid on an NMR time scale has been questioned, and, indeed if the two tautomers were rapidly exchanging, the spectra would not appear as it does. There would be only two multiplets and no peak at 8.6 delta, as was observed for compound 11.

Purification Problem and Solution

Vacuum subliming the phthalocyanine products is time consuming. Therefore, the research plan was altered to make the products soluble in solvents which would allow better purification of the phthalocyanines. To that end, the following synthetic path (fig. 9) to produce compound 36 from 32 was undertaken. A compound with two long chains would allow all the compounds being synthesized to be soluble in the solvents necessary to purify and characterize the materials.

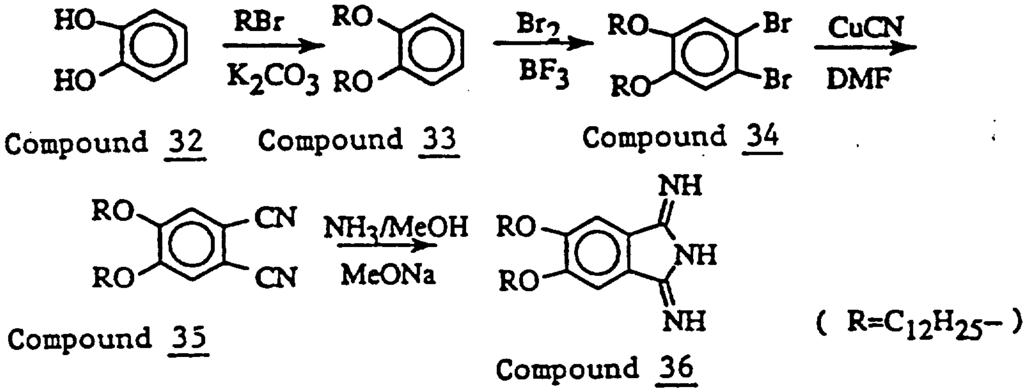
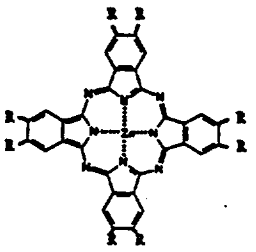


Figure 9. The synthetic path to produce compound 36 from compound 32.

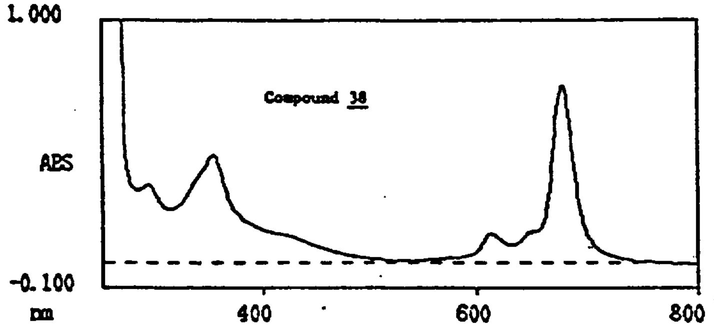
The first step involved the alkylation of dihydroxy benzene which went in virtually quantitative yield. The bromination of 1,2-didecyloxybenzene to produce 1,2-didecyloxy-4,5-dibromobenzene and recrystallization also went in very high yield. This material was reacted with copper cyanide to produce 1,2-didecyloxy-4,5-dicyanobenzene. This material was reasonably stable and was only reacted to form compound 36 shortly before it was needed.

Compound 36 was then heated in 2-N,N-dimethylaminoethanol at 140 °C to produce a green single-ringed phthalocyanine, compound 37. The same procedure was also repeated with zinc acetate which was present to produce the zinc metalated system, compound 38. Both systems were chromatographed and spectra obtained. The nonmetalated phthalocyanine will be an impurity in all synthetic preparations of the two ring systems and nonsymmetric phthalocyanines. Therefore, its characterization was critical, and it is one of the compounds being evaluated for the UV protection of plastics.

The single-ringed phthalocyanine, compound 37, produced a spectra in good agreement with that from similar molecules in the literature. The spectra from compound 38, the zinc containing phthalocyanine, is also in excellent agreement. The Qx and Qy bands at 703 and 665 nm in compound 37 are only one Q transition at 679 nm in compound 38, since the D_{2h} symmetry of compound 37 has become D_{4h} in compound 38, resulting in only one transition ($^1A_{1g}$ to ^1E_u) (fig. 10).

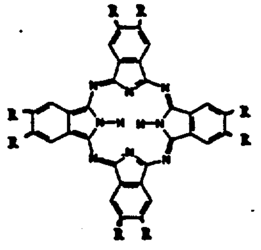


Compound 38

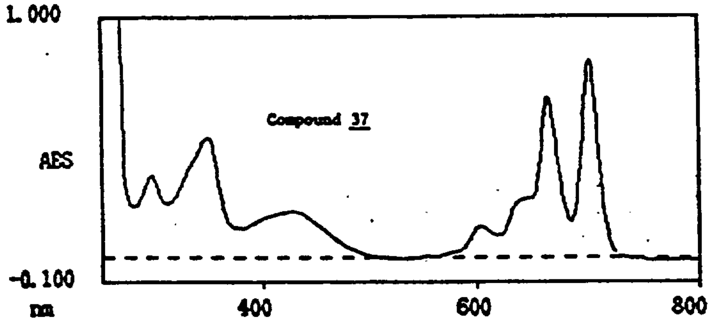


NO.	PEAK nm	PEAK ABS	VALLEY nm	VALLEY ABS
1	679.0	0.727	631.0	0.072
2	613.0	0.121	526.0	0.014
3	355.0	0.446	314.0	0.220
4	294.0	0.323	284.0	-0.300

R = -O-$(CH_2)_{11}$-CH_3



Compound 37



NO.	PEAK nm	PEAK ABS	VALLEY nm	VALLEY ABS
1	703.0	0.816	686.0	0.150
2	665.0	0.661	620.0	0.092
3	604.0	0.131	527.0	-0.002
4	427.0	0.192	382.0	0.121
5	350.0	0.501	311.0	0.225
6	297.0	0.338	280.0	0.213

Figure 10. UV/visible spectra of compounds 38 and 37.

Tetraphenyl Phthalocyanines

Tetraphenyl-phthalic anhydride, compound 39, has been utilized, which was as shown in figure 11, with phthalic anhydride heated in urea to synthesize the first targeted phthalocyanine compound 43. The synthesis of the octaphenylphthalocyanine shown in figure 11 has presumably gone as anticipated, and full confirmation of the structure through spectroscopic analysis is consistent, but purification is difficult. Absolute identification of the product as compound 43 has not been made due to impurities. The product is green, unlike the parent which is blue. The blue color of the standard phthalocyanine is in part due to two phthalocyanines coupling through their pi systems. In the case of the octaphenylphthalocyanine, the presence of the eight phenyls at a 45° angle precludes the approach to a coupling distance according to SIBYL modeling. The octaphenylphthalocyanine was sublimated, but difficulty in sublimation precluded its further purification. The distance between the planar rings will be of particular interest. We obtained Magic Angle spinning NMR spectra of this compound to help confirm the structure. The use of Magic Angle spinning is required since the compound lacks solubility in any reasonable solvent. The spectra was consistent but lacked enough definition to be absolutely conclusive.

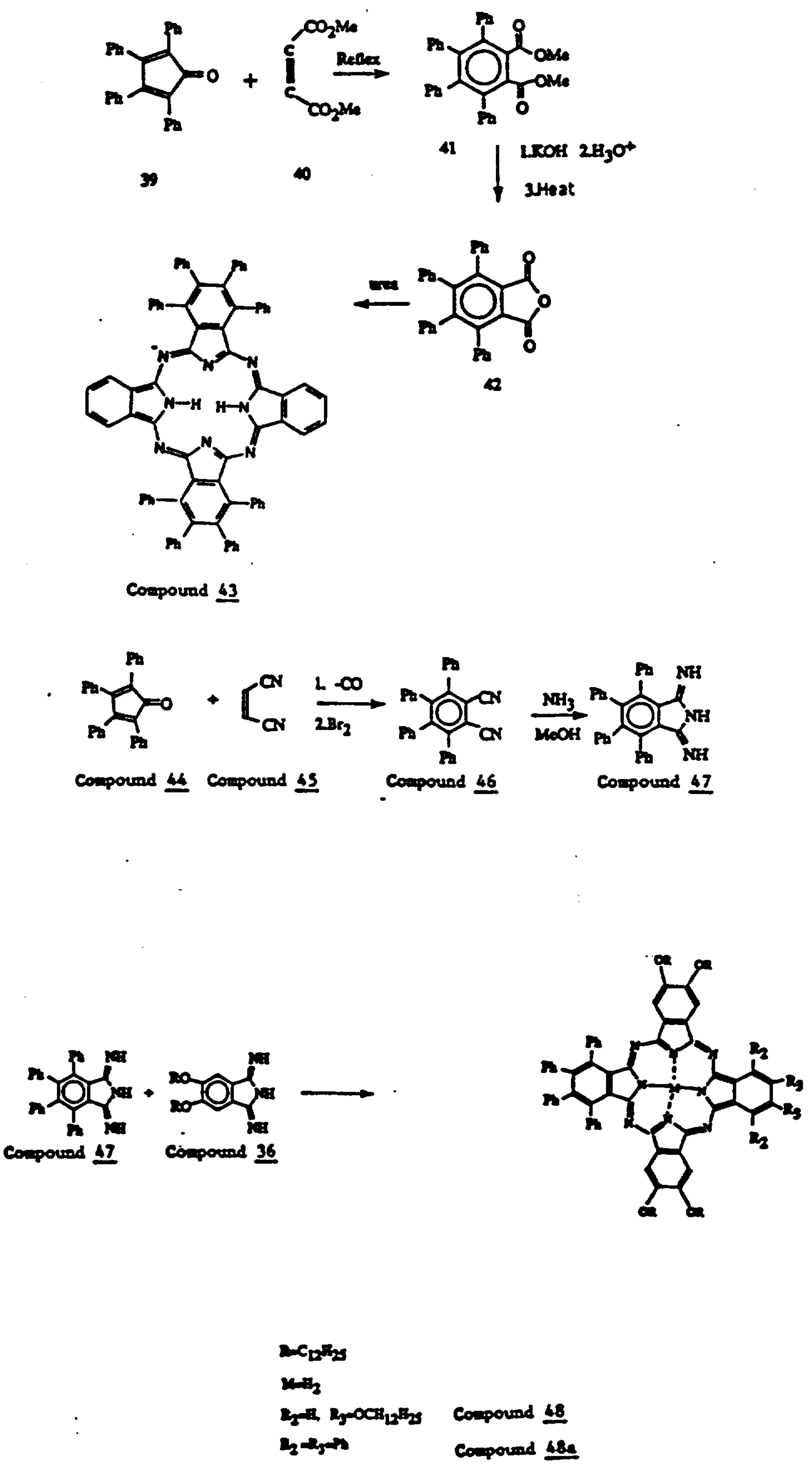


Figure 11. The synthesis schemes to prepare compounds 43 and 48.

To increase the yield of tetraphenylphthalate incorporation and to ease the purification problem, compound 48 was targeted. The approach was to make the key intermediate 47 from compound 44. This approach went well from compound 44 to 46. The last step went slowly, and compound 47 was found to be somewhat unstable. Compound 48 was prepared using the intermediate compound 47 and compound 36. The phthalocyanine, compound 48, was the major product other than the expected compound 37. The large steric hindrance of the tetraphenyl group reduces the amount of bis incorporation, compound 43 with dodecyl chains. We have worked out separation techniques using normal and size exclusion chromatography to purify this material. The UV/visible spectra of this material is shown in figure 12.

Compound 48 was then metalated with cobalt in toluene and purified compound 48*Co. The spectra below illustrates the collapse of the splitting and a spectral shift. It should be noted that this compound is much more blue than compound 48.

AMPAC Calculations on Phthalocyanines

The newest version of AMPAC was obtained by an MNDO and AM1 quantum mechanical package used to determine the electronic energetics of a structure. The AMPAC program was installed on our Silicon Graphics computer and on the IBM 6000 RISC system. AMPAC has been verified as being in correct working order on the Silicon Graphics computer, however, the memory limits of that computer will only allow 50 nonhydrogen atoms to be calculated. The targeted molecule has nearly 150 nonhydrogen atoms. AMPAC was successfully ported to the IBM-6000 which has six times the memory and approximately six times the speed of the Silicon Graphics computer. The IBM allows a matrix of the full 150 atoms to be calculated.

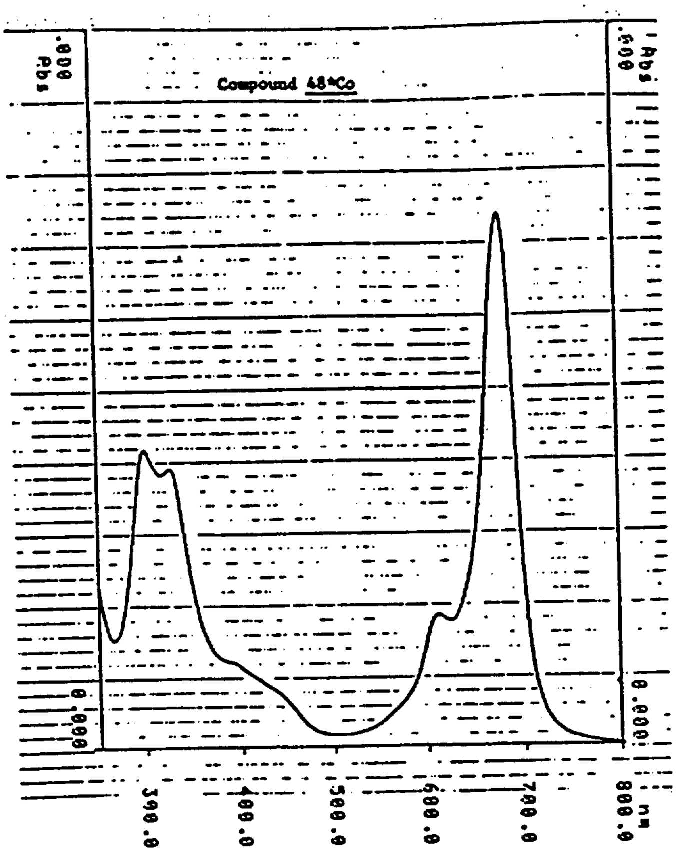
Compounds 49 to 57 were molecularly modeled using either Sybyl or Alchemy and MNDO run to GNORM = 0.1. The values for the heats of formation and ionization potential are given with the structures. The electron density matrix and bond order were calculated and indicate good stability for all the compounds. Therefore, compounds 49 to 57 should be stable if they can be constructed. It does not mean that by using conventional techniques they can be synthesized. Thus far, we have been able to construct relatives of compounds 49, 50, 51, 52, 56, and 57.

Below are the results of optimization for phthalocyanine by MNDO to GNORM = 0.5 level. The structural assignment, which was set by first using SYBYL to define the coordinate, input to AMPAC and then optimized by AMPAC. The agreement with coordinates is excellent. Thus, the program is very useful and reliable.

PHTHALOCYANINE $C_{32}H_{18}N_8$

HEAT OF FORMATION = 258.441407 KCAL
GRADIENT NORM = 0.546150
DIPOLE = 6.54579 DEBYE
NO. OF FILLED LEVELS = 93
IONIZATION POTENTIAL = 7.031705 EV
MOLECULAR WEIGHT = 514.548
SCF CALCULATIONS = 704
COMPUTATION TIME = 4,964.57 SECONDS

GRADIENTS GNORM=0. T=18,000 BONDS XYZ



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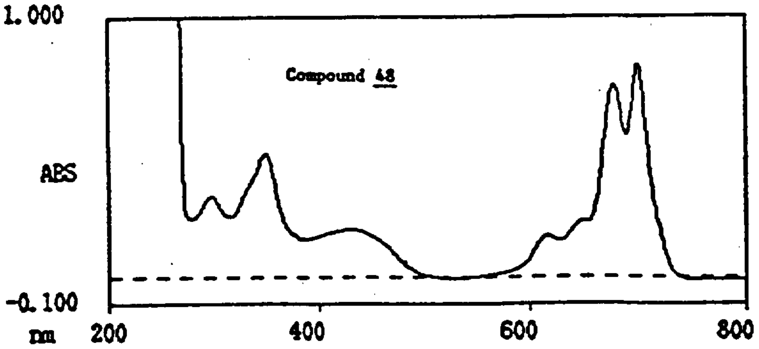
TITLE: TETRAPC(CO)                          9:33 PM   7/29/92
SCAN SPEED:  120.0 nm/min                   RESPONSE: MEDIUM
BANDPASS: 2.00nm

 NO.           PEAK                           VALLEY
  1   679.6 nm    0.7372 Abs    625.2 nm    0.1735 Abs
  2   613.2 nm    0.1918 Abs    585.4 nm    0.0159 Abs
  3   329.8 nm    0.3976 Abs    320.4 nm    0.3794 Abs
  4   382.4 nm    0.4145 Abs    265.6 nm    0.1497 Abs
```



	PEAK		VALLEY	
NO.	nm	ABS	nm	ABS
1	700.0	0.816	689.0	0.545
2	678.0	0.740	627.0	0.143
3	615.0	0.162	525.0	-0.002
4	430.0	0.186	387.0	0.148
5	349.0	0.475	314.0	0.235
6	297.0	0.314	279.0	0.228

Figure 12. The UV/visible spectra of compound 48.

The following is a list of the atoms and their bond lengths and charges. They are all consistent with the x-ray structure.

PHTHALOCYANINE

H	0.000000	0	0.000000	0	0.000000	0	0	0	0	0.2500
N	0.998794	1	0.000000	0	0.000000	0	1	0	0	–0.3493
C	1.410083	1	123.274504	1	0.000000	0	2	1	0	0.3216
C	1.490919	1	105.272354	1	–171.422793	1	3	2	1	–0.0785
C	1.392891	1	131.552656	1	176.745284	1	4	3	2	0.0194
H	1.089965	1	121.824595	1	–0.454258	1	5	4	3	0.0852
C	1.420394	1	118.347526	1	179.539485	1	5	4	3	–0.0500
H	1.091072	1	119.047973	1	179.986936	1	7	5	4	0.0706
C	1.398585	1	121.039694	1	–0.036030	1	7	5	4	–0.0499
H	1.091035	1	119.923550	1	–179.983607	1	9	7	5	0.0706
C	1.420469	1	121.032944	1	–0.007165	1	9	7	5	0.0193
H	1.089950	1	119.826271	1	–179.943066	1	11	9	7	0.0852
C	1.392879	1	118.360722	1	0.047439	1	11	9	7	–0.0783
C	1.410049	1	123.271596	1	–177.622484	1	2	1	3	0.3215
N	1.304946	1	129.481435	1	–10.283670	1	14	2	1	–0.2975
C	1.390894	1	126.278698	1	–3.972449	1	15	14	2	0.2258
C	1.487877	1	123.205437	1	176.588227	1	16	15	14	–0.0970
C	1.392105	1	134.063507	1	–2.391322	1	17	16	15	0.0179
H	1.089571	1	121.848800	1	–0.180035	1	18	17	16	0.0747
C	1.418637	1	118.186206	1	179.791620	1	18	17	16	–0.0689
H	1.090850	1	119.145540	1	–179.981660	1	20	18	17	0.0635
C	1.400309	1	121.059488	1	–0.001801	1	20	18	17	–0.0465
H	1.091063	1	119.749755	1	–179.967749	1	22	20	18	0.0638
C	1.419161	1	121.185197	1	0.039258	1	22	20	18	–0.0014
H	1.089607	1	119.958121	1	179.976404	1	24	22	20	0.0802
C	1.392589	1	118.232935	1	–0.013089	1	24	22	20	–0.0549
C	1.489614	1	133.420450	1	179.707829	1	26	24	22	0.1374
N	1.327737	1	125.164776	1	–6.015470	1	16	15	14	–0.3500
N	1.303113	1	125.394391	1	–1.015780	1	27	26	24	–0.1735
C	1.377829	1	127.430095	1	–178.034930	1	29	27	26	0.0849
C	1.434558	1	125.793628	1	169.004139	1	30	29	27	–0.0548
C	1.429561	1	132.833780	1	1.924553	1	31	30	29	–0.0096
H	1.089654	1	120.087762	1	0.359922	1	32	31	30	0.0670
C	1.383207	1	118.919548	1	–179.822116	1	32	31	30	–0.0700
H	1.091000	1	120.352888	1	–179.758491	1	34	32	31	0.0547
C	1.435376	1	121.285091	1	0.235642	1	34	32	31	–0.0700
H	1.090862	1	118.345146	1	179.995505	1	36	34	32	0.0546
C	1.383308	1	121.292493	1	–0.015378	1	36	34	32	–0.0095
H	1.089717	1	120.997717	1	179.956370	1	38	36	34	0.0670
C	1.429607	1	118.921141	1	–0.219604	1	38	36	34	–0.0549
C	1.434618	1	132.876862	1	179.825074	1	40	38	36	0.0851
N	1.394135	1	106.793445	1	179.321474	1	41	40	38	–0.1646
H	0.997840	1	124.007711	1	–172.236465	1	42	41	40	0.2354
N	1.377948	1	125.814341	1	–1.890570	1	41	40	38	–0.1736
C	1.303103	1	127.421565	1	–168.947802	1	44	41	40	0.1376

C	1.489540	1	125.363889	1	178.087614	1	45	44	41	–0.0550
C	1.392497	1	133.409538	1	1.023328	1	46	45	44	–0.0013
H	1.089640	1	121.818556	1	0.287947	1	47	46	45	0.0802
C	1.419191	1	118.215595	1	–179.701601	1	47	46	45	–0.0465
H	1.091119	1	119.048320	1	–179.990197	1	49	47	46	0.0638
C	1.400311	1	121.190045	1	0.032844	1	49	47	46	–0.0689
H	1.090782	1	119.816805	1	179.961353	1	51	49	47	0.0635
C	1.418710	1	121.064798	1	–0.072158	1	51	49	47	0.0179
H	1.089594	1	119.962208	1	–179.962995	1	53	51	49	0.0747
C	1.392050	1	118.174891	1	0.018248	1	53	51	49	–0.0970
C	1.487911	1	134.061610	1	–179.771437	1	55	53	51	0.2258
N	1.327761	1	111.589676	1	–179.890044	1	56	55	53	–0.3500
N	1.304970	1	129.470943	1	10.332903	1	3	2	1	–0.2976
O	0.000000	0	0.000000	0	0.000000	0	0	0	0	

This structure is minimized with zinc as the center element for the standard phthalocyanine as defined using x-ray coordinates.

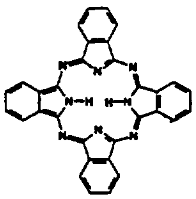
PHTHALOCYANINE-CO/ZN $C_{32}H_{16}N_8Zn$

HEAT OF FORMATION = 253.641375 KCAL
GRADIENT NORM = 0.066891
DIPOLE = 5.99888 DEBYE
NO. OF FILLED LEVELS = 93
IONIZATION POTENTIAL = 6.683682 EV
MOLECULAR WEIGHT = 577.912
SCF CALCULATIONS = 260
COMPUTATION TIME = 2,480.54 SECONDS
GRADIENTS GNORM=0. T=18,000 BONDS DENSITY XYZ

The next structure is the bisphthalocyanine complexes with anthracene core. The results indicate that the structure should be relatively stable.

ANTH-DI-PHTHOLOCYNINE $C_{66}H_{34}N_{16}$

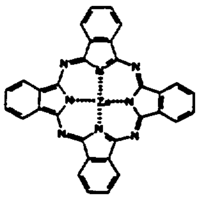
HEAT OF FORMATION = 541.250239 KCAL
GRADIENT NORM = 19.548030
DIPOLE = 17.97050 DEBYE
NO. OF FILLED LEVELS = 189
IONIZATION POTENTIAL = 6.842447 EV
MOLECULAR WEIGHT = 1,051.102
SCF CALCULATIONS = 169
COMPUTATION TIME = 15,029.95 SECONDS
GRADIENTS GNORM=20 BONDS T=18,000 BONDS XYZ



Compound 49

H.F. = 258.44 Kcal

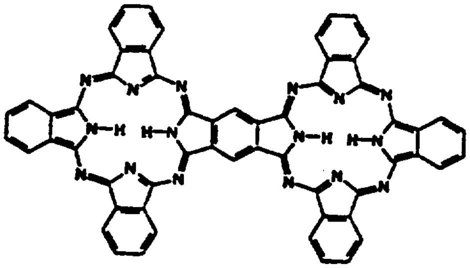
I.P. = 7.032 EV



Compound 50

H.F. = 253.64 Kcal

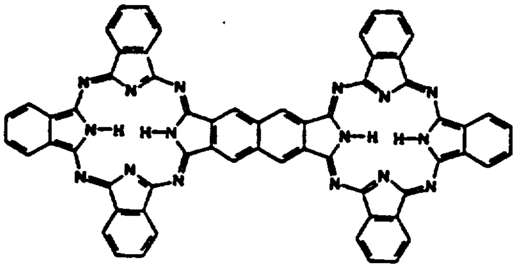
I.P. = 6.684 EV



Compound 51

H.F. = 498.68 Kcal

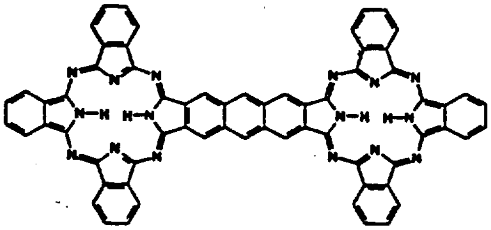
I.P. = 7.176 EV



Compound 52

H.F. = 512.35 Kcal

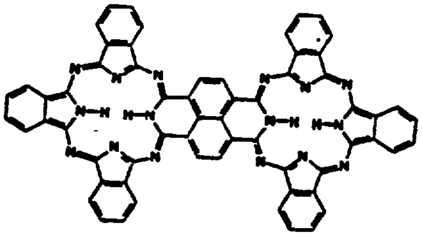
I.P. = 7.139 EV



Compound 53

H.F. = 535.35 Kcal

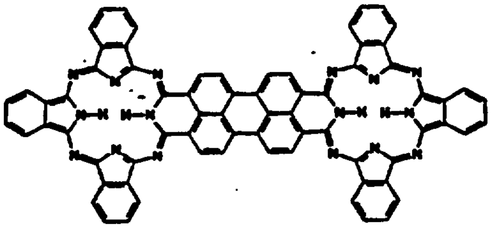
I.P. = 6.839 EV



Compound 54

H.F. = 513.17 Kcal

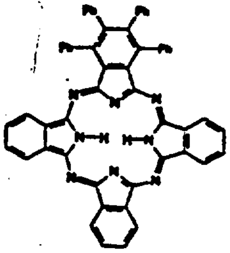
I.P. = 7.110 EV



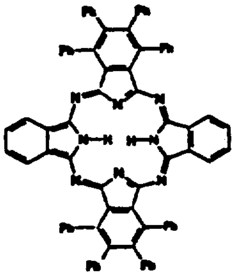
Compound 55

H.F. = 556.90 Kcal

I.P. = 7.050 EV



Compound 56



Compound 57

Synthesis of Bisphthalocyanines

The original proposal targeted structures 54 and 55 as two bisphthalocyanines to possibly synthesize. Compounds of the type represented by compound 51 have been published in the literature and are very stable. Compound 55 was targeted as our first goal. The attempts to produce 55 resulted in the formation of the bisimide compound 4. This reaction path was confirmed by utilizing the heating of just urea and compound 2 to produce the same identical product as that when phthalic anhydride was included. Therefore, compound 55 cannot be prepared by this classical methodology. Compounds 52 and 53 were targeted, as well as pursuing the naphthalene model for compound 55 to produce compound 6.

Benzene Core

The first bisphthalocyanine synthesized was based upon pyromellitic dianhydride. This compound is similar to that reported in the literature with the exception of the alkyl chain length, which is two carbons longer. This octadodecyl system, compound 51a, was prepared by the method outlined in figure 13. Compound 58 was converted to compound 61 which again is a key intermediate in the formation of phthalocyanines. Compound 61 was then heated with compound 36, producing a mixture of compound 37 and 51a, the single- and double-ring phthalocyanines.

The two-ringed system is soluble in the typical solvents used to dissolve the polymers used in coatings, as well as being compatible with the polymers themselves. A separation technique has been working out, using size exclusion chromatography which is capable of resolving the single- from the double-ringed phthalocyanine system. The use of size exclusion chromatography beads for preparative separation of these two materials worked well. The UV/visible spectra of the mixture indicate a great similarity between the two compounds.

Naphthalene Core

The synthesis of the naphthalene core used in making compound 52a is shown in figure 15, compounds 62 to 67. The synthetic pathway worked well except for conversion of 65 to 66. Here the purification of the produce was difficult. Conversion of 66 is the key intermediate 67 went well. Compound 67 was then heated with compound 36 to produce compound 52a and compound 37, the double- and single-ringed systems. The separation of the two compounds was again accomplished with size exclusion chromatography. The spectra agreed well with the proposed structure as did its molecular weight. The UV/visible spectra is given in figure 16. This synthesis represents the first naphthalene core bisphthalocyanine made.

Anthracene Core

Three major approaches were made to synthesize an anthracene core, compound 83. These are depicted in figures 17 and 18 in structures 62 to 83. The object was to synthesize compound 53a.

The first approach has progressed to structure 64, and, on a small scale, compound 68 has been made. This approach is of low yield and somewhat poor, but effective. The purification of compound 68 makes this approach somewhat less attractive.

The second approach is far more elegant, utilizing a double Diels Alder of 71 and 72 to produce, followed by air oxidation cleanly produced the dione 73. The oxidation of 73 using chromate in liquid

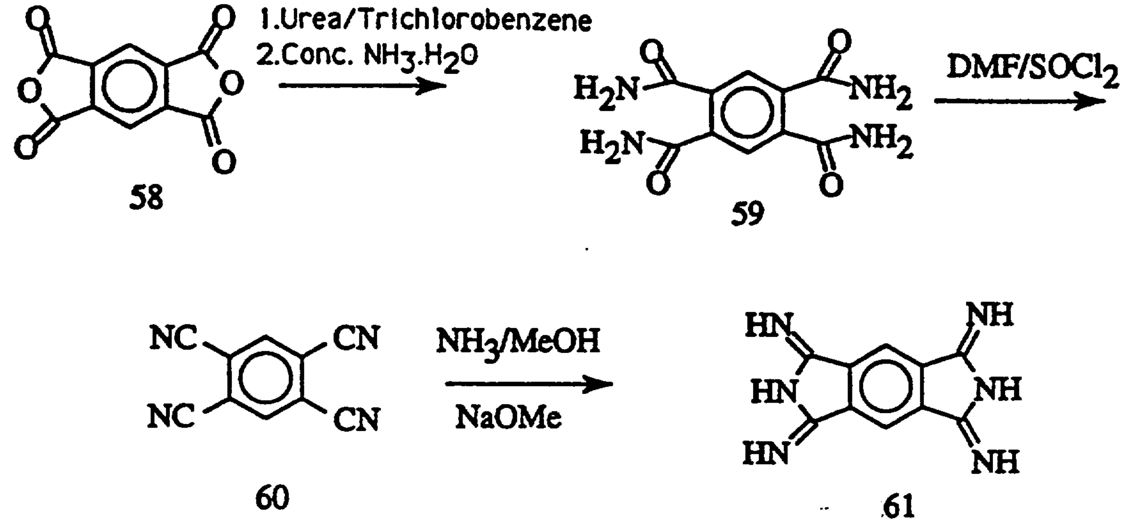
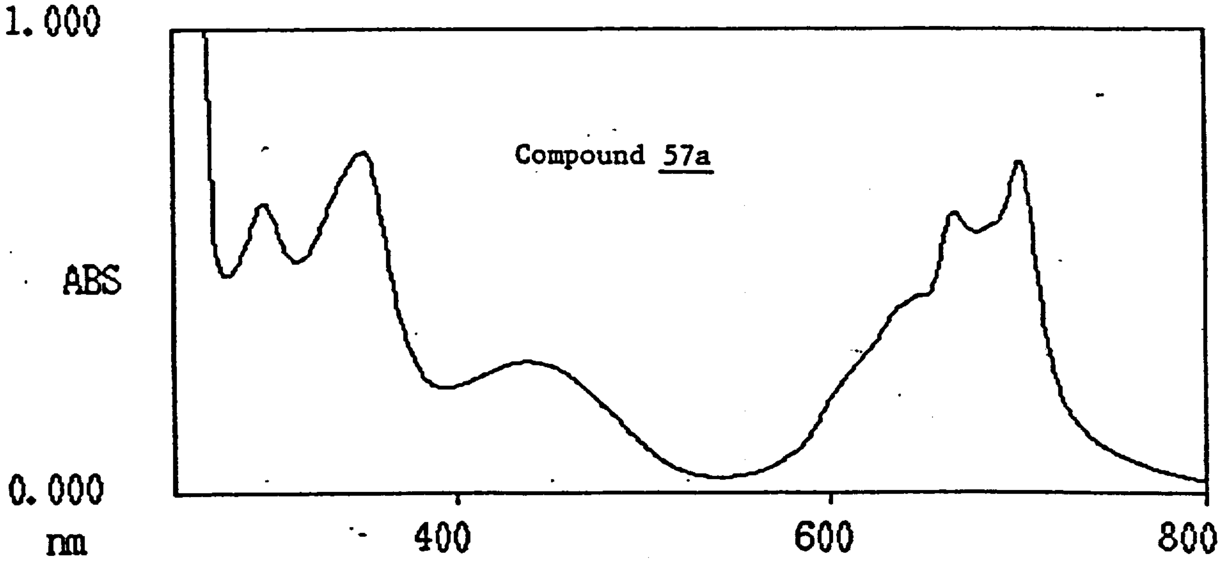


Figure 13. The preparation method of oxtadodecyl system compound 51a.



```
          PEAK                  VALLEY
     --------------        --------------
NO.     nm      ABS           nm      ABS
 1    702.0   0.713         678.0   0.559
 2    667.0   0.600         541.0   0.033
 3    438.0   0.282         394.0   0.228
 4    351.0   0.734         314.0   0.499
 5    297.0   0.624         277.0   0.468
```

Figure 14. UV/visible spectrum of compound 57a.

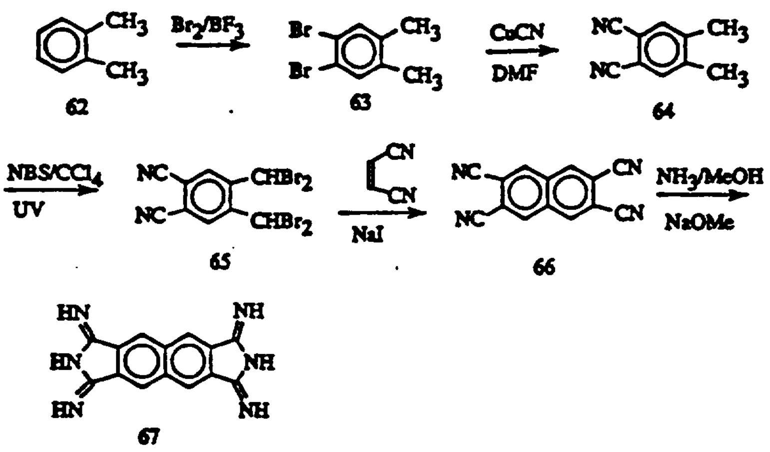
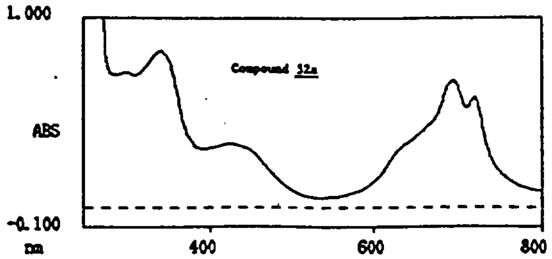


Figure 15. The synthesis scheme of compound 52a.



NO.	PEAK nm	PEAK ABS	VALLEY nm	VALLEY ABS
1	720.0	0.583	710.0	0.529
2	694.0	0.671	535.0	0.055
3	424.0	0.339	393.0	0.315
4	341.0	0.827	310.0	0.700
5	299.0	0.715	288.0	0.701

Figure 16. UV/visible spectrum of compound 52a.

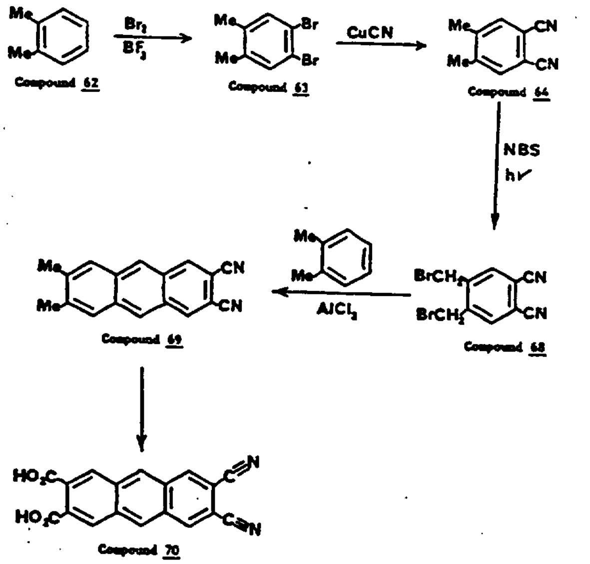


Figure 17. The first approach to synthesize compound 53a.

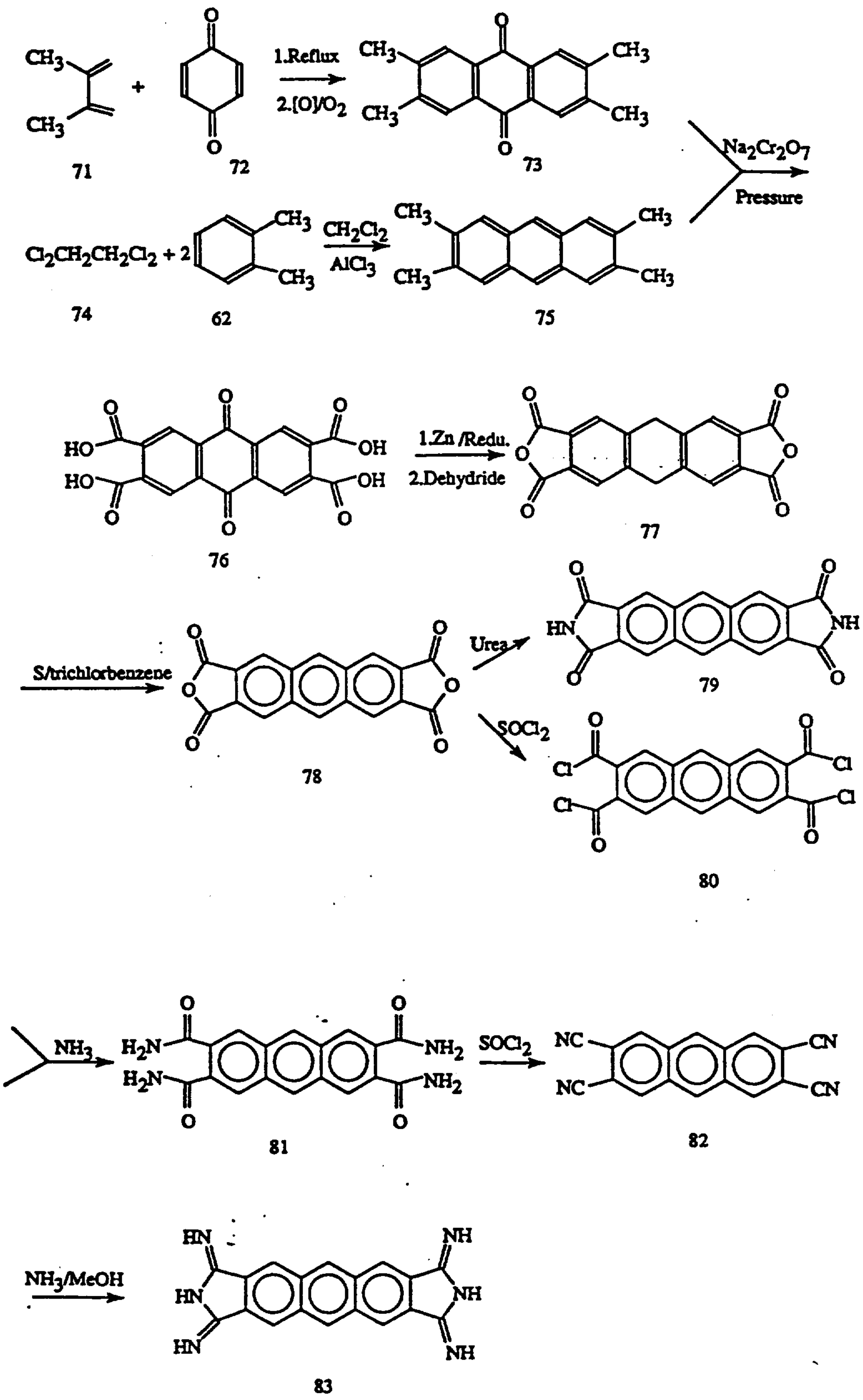


Figure 18. The second and third approach to synthesize compound 53a.

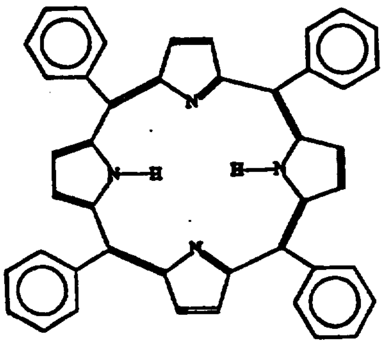
carbon dioxide produced compound 76. Compound 76 was also produced from a tetra-Friedel Craft reaction on orthoxylene followed by chromate oxidation in liquid carbon dioxide. The two approaches were combined to increase the amount of compound 76.

Compound 76 was reduced and then dehydrated to form the bis-anhydride compound 77. Aromatization and purification by sublimation produced the targeted anhydride compound 78. It was planned that this less reactive compound would be converted to compound 83. All attempts to convert this material to compound 83 have failed. Compound 83 was reacted with compound 36 in urea in hopes of the formation of compound 53a, however, no bisphthalocyanine was produced.

Plastic UV Protection

The design of the test procedure for evaluation of the phthalocyanines for protecting plastics from UV damage are being made with no inhibitor, phthalo blue (commercial) and phthalo green (commercial) as standard materials for comparison with new synthesized pigments. The materials are being tested as to gloss, color, molecular weight distribution, and IR. After exposure to UV, the materials will likewise be evaluated by the same techniques.

The phthalo blue (blue), phthalo green (green), and polystyrene standard (control) glass test panels on samples, as well as, the single-ringed phthalocyanine compound 37 (DD green) based on 1,2-didodecyloxy-4,5-dicyanobenzene, have been prepared for the photodegradation study. Polystyrene with a 3-percent loading of the pigments which are insoluble and 1.5-percent pigment have been used for the newly synthesized soluble pigments. Polystyrene is known to yellow and degrade with UV exposure. It has been prepared in solution so that it can be applied to glass as a thin film for UV exposure. For comparison purposes, a set of samples using 0.75-percent tetraphenylporphine (TPP), compound 84 (fig. 19), has been prepared as the soluble pigment. These are carbon analogues of the phthalocyanines and are soluble in the solvent used, toluene, and do not tend to form dimers in solution due to the four phenyls being at a 45° dihedryl angle to the porphyrin ring. This pigment is maroon colored in solution or in the polymer film, but purple in the crystalline solid form. The polymer/pigment system was milled in toluene with glass beads in a pseudo-sand mill (a straight blade on a drill press). A significant cobwebbing problem has been observed with spraying due to the high molecular weight of the polystyrene used. This problem will not prevent the use of this system, but does create a mess during the spraying process. The color development was very good, but the long-term solution stability of the insoluble pigments is not good. The dispersed pigments were sprayed within hours of their being milled.



Compound 84

Figure 19. Chemical structure of tetraphenylporphine.

Results and Discussion

The samples, inside a vacuum chamber at approximately 1.0×10^{-6} torr, were exposed to UV light (equivalent to 1.5 Sun level) ranging from 200 to 1,100 nm for 100 hours at 250 °F. The total amount of UV light exposed on these samples was approximately 150 Sun level. Using black light for visible inspection of color change, it could be seen that the sample has changed to a light fluorescent color. For example, the green sample in figure 20 changed from deep, dark green to a light fluorescent green after 100 hours of exposure.

Transmittance integrated sphere diffusion reflectance was used to further study the color change of these samples. In all of the pigments except DD green (fig. 21), the UV exposed samples had a higher transmittance value than the unexposed samples. These data showed that the colors of exposed and unexposed samples were not identical. The color change in the DD green sample was relatively low compared to the other samples. These results agree very well with the visible inspection with black light.

A spectrofluorometer (model SPE-500C) was used to investigate the spectral distribution of fluorescence emitted by these samples before and after UV exposure. Emission was measured over a range from 300 to 900 nm with an excitation wavelength of 260 nm. As indicated in figure 22, UV exposure dramatically altered the fluorescence spectra of the samples. In all of the samples except TPP, the maximal peak was shifted to a higher wavelength. Except in the case of DD green and blue, the

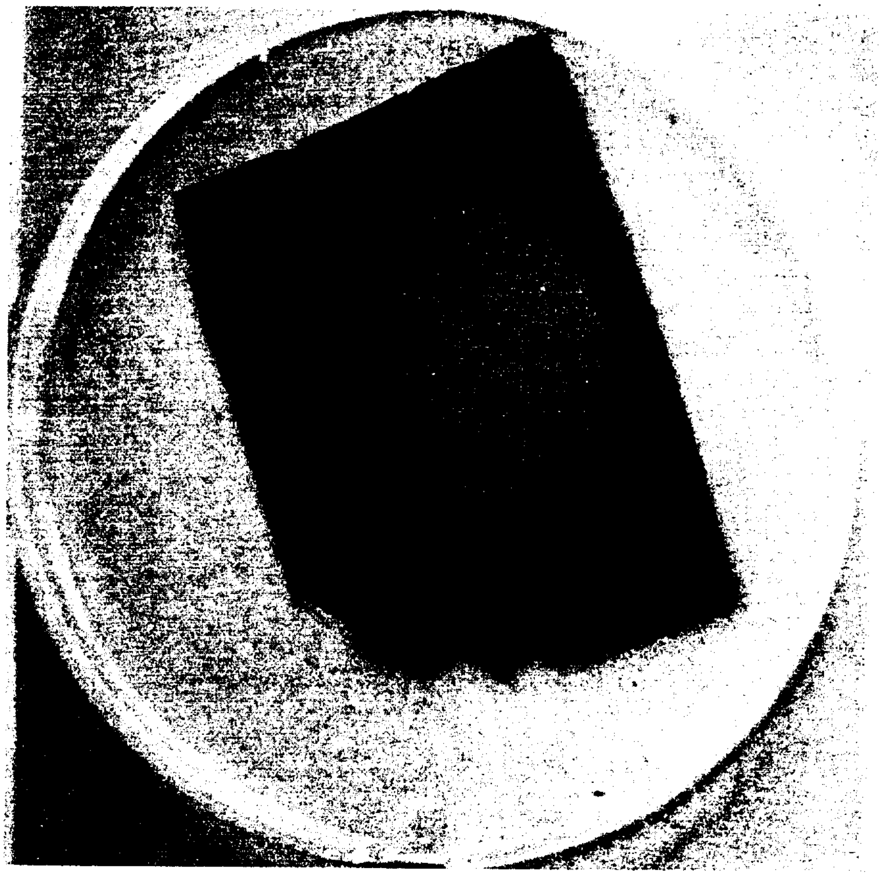


Figure 20. Black light photographic print of green sample.

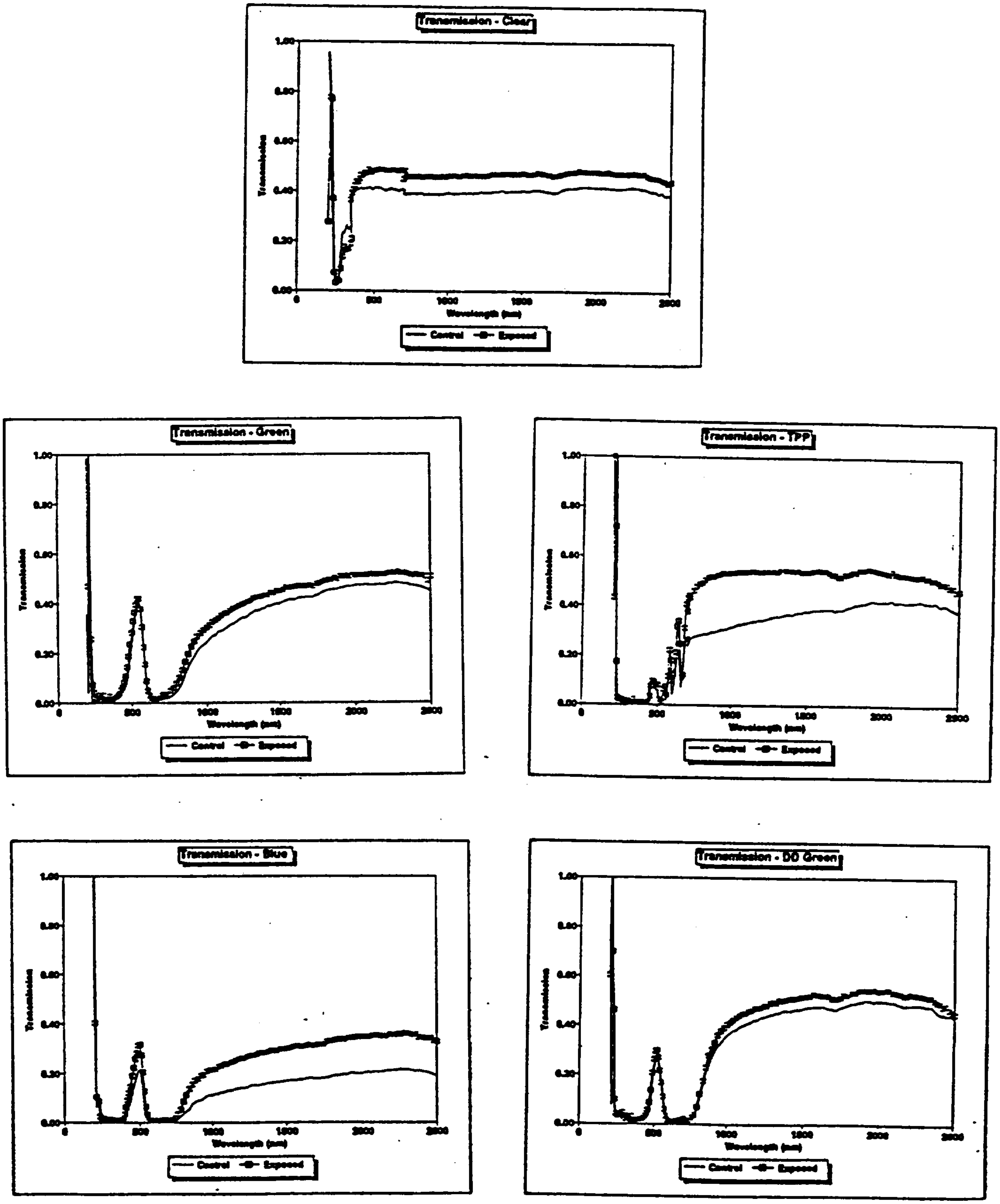


Figure 21. The transmittance spectra of control, green, TPP, blue, and DD green.

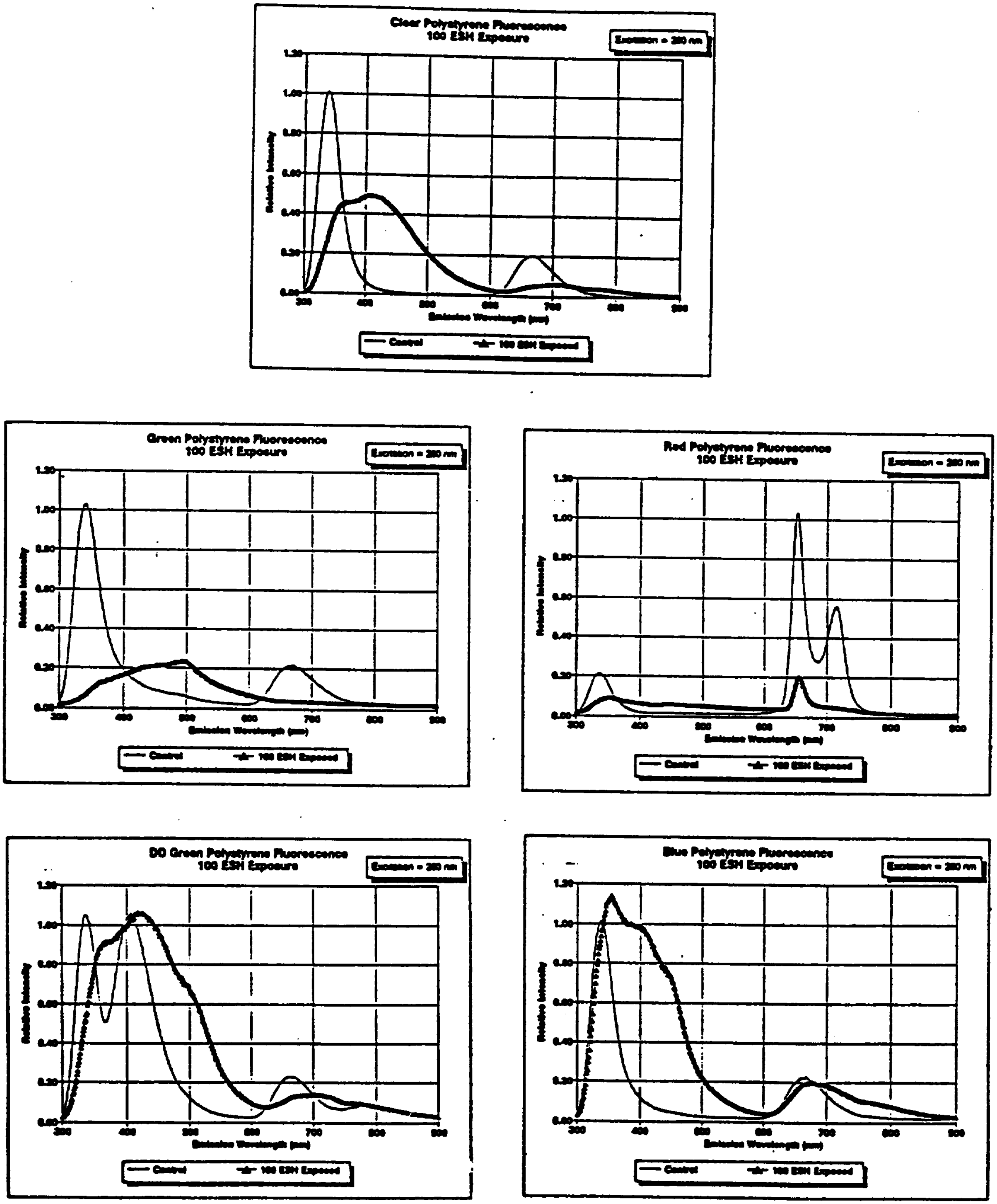


Figure 22. The fluorescence spectra of control, green, TPP, blue, and DD green.

relative intensities of the maximal peaks were greatly reduced. Before UV exposure, the control sample emitted fluorescence at 332 nm (major peak) and 666 nm (minor peak). After exposure, the internal energy-producing fluorescence was reduced, and those two bands disappeared, only one band remained—a broad band at approximately 400 nm. Before UV exposure, the fluorescence spectra for the green and blue samples were almost identical to that of the control sample. Exposure of the green sample to UV eliminated the peak at 332 and 666 nm; only one band was present—a broad band with relatively low intensity at 500 nm. The maximal peak for the blue sample changed from a sharp peak at 332 nm to a large, broad peak at 362 nm, with the relative intensity unchanged. The spectrum for TPP had two bands—a minor band at 337 nm and a double band at 644 nm and 719 nm before UV exposure. After exposure, the first peak disappeared, and the doublet became a singlet shifted to 655 nm (the relative intensity was much lower than that of the pre-exposure 644 nm peak). The fluorescence emission spectrum of DD green had a doublet with relatively the same intensity at 337 and 408 nm and a small singlet at 662 nm. After UV exposure, the doublet became a broad peak and shifted to a higher wavelength (430 nm) with the same relative intensity, and the singlet disappeared. Comparing the spectral distribution of fluorescence emitted by these samples, DD green and blue protected plastic better against UV damage than did green and TPP.

Bidirectional transmissive distribution (BTDF) data implied that the surfaces of UV exposed samples were opaque (fig. 23). Curves for exposed and unexposed samples were far apart for green, TPP, and control samples; for blue and DD green samples, they were close together, indicating much less surface change. The TPP sample showed the most change.

Differential scanning calorimetry (DSC) was used to measure the amount of energy absorbed or released by the samples as they were heated. Thermal activity decreased in DD green, blue, TPP, and control samples after UV exposure, showing that phase transition is required more in exposed samples than in unexposed samples. Green samples behaved differently—thermal activity increased after exposure to the UV light. Thermogravimetry analysis (TGA) was used to measure the change in mass of the samples as they are heated. UV exposure did not change the decomposition profile of any sample as it was exposed to a linearly increasing temperature.

In the presence of oxygen, polystyrene turns from clear to yellow when exposed to UV light, indicating that the polymer undergoes photo-oxidation to form ketone and acid (24, 25). However, when oxygen is absent, UV exposure does not cause the polymer to undergo this reaction. The infrared spectra of UV exposed samples did not show any band that indicated the presence of hydroxyl (-OH) group or carbonyl (-C-) group. Rather, the infrared spectra of these samples were identical before and after UV exposure. Evidently, the polymer did not undergo UV degradation. A certain reaction must take place in the polymer matrix itself when the sample is exposed to UV light, but these reactions did not yield any product which could be detected or distinguished by infrared spectroscopy. When these samples were dissolved in tetrahydrofuran (THF) for gel permeation chromatography (GPC), a small string was observed on UV exposed samples. The string residue which was insoluble in THF proved that the polymer undergoes cross linking when exposed to UV light. These strings were examined by Fourier transform infrared (FTIR) spectroscopy and compared to the control spectrum. Structurally, the IR spectra of the string residue and the polymer are identical. The IR technique itself cannot detect any cross-linkage bonding in the polymer.

Solution of polymer and pigment in THF were subjected to GPC analysis for molecular weight determination. Interestingly, all the UV exposed samples had higher molecular weight than their unexposed counterparts. The percent increase in molecular weight of the polymer varied with the type of

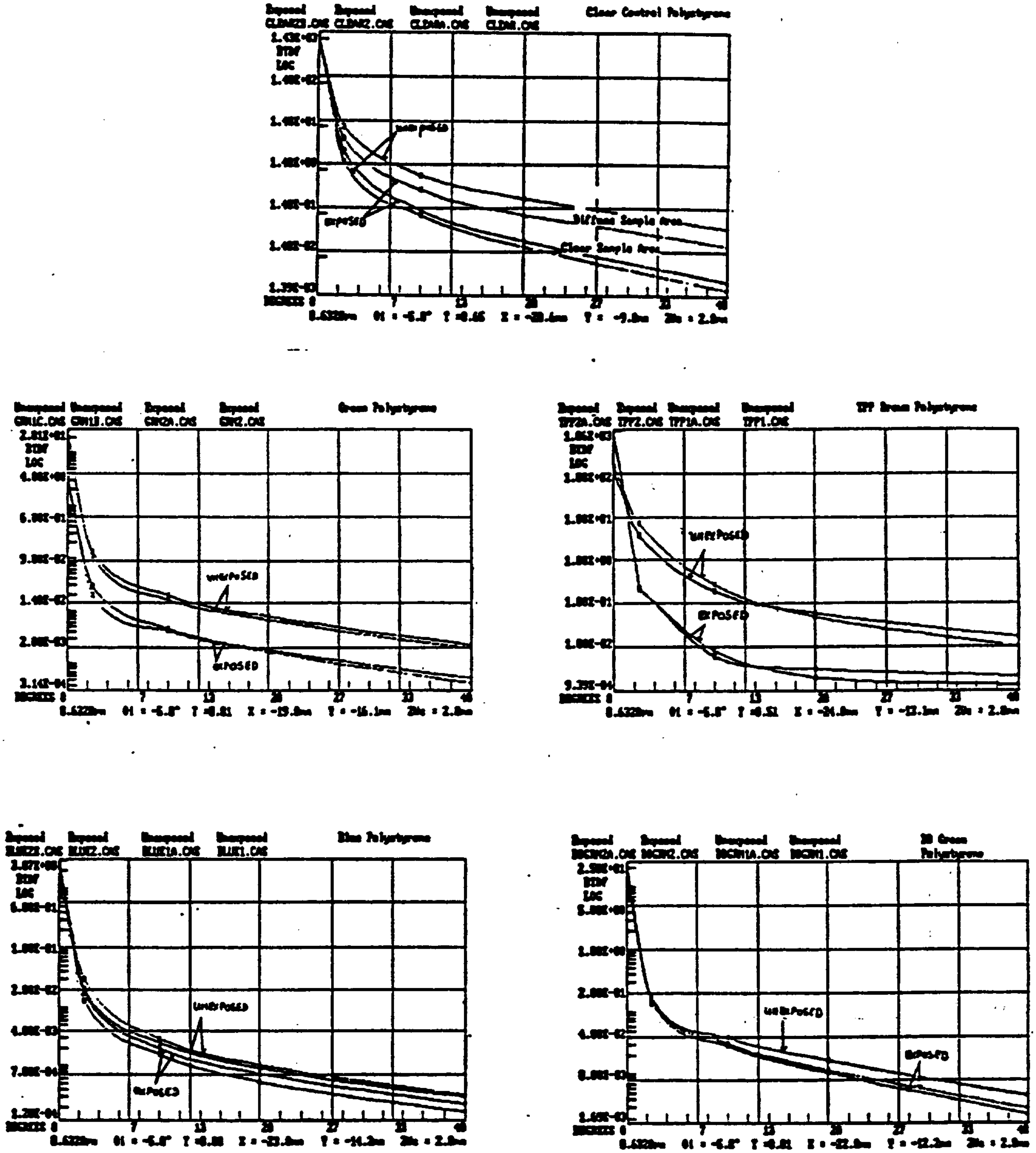


Figure 23. The BTDF curves of control, green, TPP, blue, and DD green.

pigment. Molecular weight increase in the control and green samples were very similar—16 and 15 percent, respectively. TPP had the greatest increase (approximately 22 percent), and the blue sample had the smallest increase (8 percent). The DD green sample increased only 11 percent. When exposed to UV light under a vacuum, polystyrene undergoes further polymerization. Depending on the pigment, it either increases or decreases the polymerization process. Further research is required to understand the mechanism of UV polymerization of polystyrene in a vacuum.

EXPERIMENTAL

Matheson high-purity argon was used to maintain inert atmosphere conditions. Infrared (IR) spectra were recorded on a Perkin-Elmer 1750 FT-IR spectrophotometer using a KBr disk. Nuclear magnetic resonance (NMR) spectra were recorded on JEOL FX-100 multinuclear NMR using deuteriochloroform as the solvent and tetramethyl silane as the internal standard. The positions of the signal are reported in g units. (The splittings of the signals are described as singlets (s), doublets (d), triplets (t), quartets (q), or multiplets (m).) The visible-UV spectra were recorded on a Hitachi 2000 spectrometer. Melting points (mp) were determined using a Fisher-Johns melting apparatus. Thin-layer chromatography (TLC) was performed using alumina as the absorbent. Flash chromatography was performed using silica gel of particle size (40 to 63 µm). All solvents were freshly distilled before use. DMF was passed through an alumina column before use. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

1,2-Bis(dodecyloxy)benzene (33)

From a solution of 44 g (0.40 mol) catechol in 150 mL of DMSO, dissolved oxygen was removed by repeated evacuation followed by admission of nitrogen. 1-bromododecane (210 g, 0.84 mol) was added and the two-phase system again deoxygenated. 125 g (0.9 mol) of K2CO3 was then added and the mixture was heated at 100 °C in a dry nitrogen atmosphere with mechanical stirring. After 8 h, 500 mL of water and 200 mL of methylene chloride were added. The organic layer was separated and the aqueous layer extracted with 3 by 50 mL of chloroform. The combined organic extracts were washed with 200 mL of water, dried over MgSO4, and concentrated under vacuum. Excess 1-bromododecane was removed by distillation under reduced pressure (134 to 135 C; 6 torr). The remaining light-brown solid was recrystallized from acetone (4 to 7 C). Yield 134 g (75 percent) of a white solid; m.p. 51 C. IR (KBr): 750 (o-substituted benzene), 1020 (ArOC) cm-1. 1HNMR:0.9(t,6H, CH3), 1.3(s,br, 40H,CH2), 3.90(t, 4H,OCH2), 6.9(s,4H, ArH).

1,2-Dibromo-4,5-bis(dodecyloxy)benzene (34)

Compound 33 (102 g, 0.23 mol) and a catalytic amount of BF_3 was dissolved in 500 mL of chloroform. To this solution, 26 mL (0.50 mol) of Br_2 in 50 mL of methylene chloride was added over 1 h, the first half at 0 °C, the second half at room temperature. The mixture was stirred for 2 h at 25 °C to complete the reaction, which was checked by TLC. The reaction mixture was washed with 10-percent aqueous NaHSO3, 10-percent aqueous NaHCO3, and twice with water. The extract was dried over $MgSO_4$ and evaporated to dryness. Recrystallization from methylene chloride yielded a white powder. Yield 131 g (94 percent); m.p. 53.8 C. IR (KBr): 654 (ArBr), 1021 (ArOC) cm-1.1HNMR: 0.90 (t,6H,CH3), 1.3 (s,br,40H,CH2), 3.93 (t,4H,OCH2), 7.07 (s,2H,ArH).

1,2-Dicyano-4,5-bis(dodecyloxy)benzene (35)

A mixture of 202 g (0.33 mol) 1,2-dibromo-4,5-bis(dodecyloxy)-benzene (34) and 104 g (1.16 mol) CuCn was refluxed in 1,400 mL DMF and 130 mL pyridine for 6 h under an atmosphere of dry nitrogen. After being cooled, the reaction mixture was poured into 4:1 concentrated ammonium hydroxide and air was bubbled through the solution for 20 h. The remaining solid was suction-filtered over sintered glass. The residue was washed with 10-percent aqueous ammonia until the filtrate was colorless. Subsequently, the solid was washed with water until the washings were neutral. The dry, crude product was extracted with ether for 48 h using a soxhlet apparatus. The extract was evaporated to dryness, and the product was recrystallized from cyclohexane. The purity of the product was checked with TLC(SiO2:eluent CH3, Rf=0.5). Yield 78 g (47 percent); m.p. 107 C. IR(KBr):2229(CN), 1095(ArOC) cm-1.1H NMR:0.88(t,6H,CH3), 1.5(s,br,40H, CH2), 4.05(t, 4H,OCH2), 7.11(s,2H,ArH). Analysis: C32H52N2O2 (496.8), calc. (percent): C,77.36;H,10.55;N,5.64. Found (percent): C, 76.30;H,9.89;N,6.34.

1,3-Diimino-5,6-bis(dodecyloxy)-isoindoline (36)

A rapid stream of gaseous ammonia was bubbled through a solution of 5 g (0.01 mol) 1,2-dicyano-4,5-bis(dodecyloxy)benzene (3) and 50 mg sodium methoxide in 50 mL absolute methanol at room temperature for 1 h. The solution was heated at reflux for an additional 4 h, while the addition of ammonia was continued. At the end of addition, a precipitate was formed which was collected by suction after standing overnight and washed with small amounts of cold methanol; yield:5.1 g (98 percent); light green crystals which decomposed at 125 °C with green color (from methanol). IR(KBr):3215(N-H); 1602(C-N); 1553(C-N); 1039(ArOC)cm-1.

Pyromellitamide

A mixture consisting of 20 g (0.09 mol) of pyromellitic anhydride, 18 g (0.3 mol) of urea, and 135 g of trichlorobenzene was heated at 130 °C for several hours, then at 150 to 160 °C for 2 h. The crude pink-colored pyromellitamide did not melt below 310 °C. Treatment of the crude amide with 150 mL aqueous ammonia at room temperature gave 15 g of nearly colorless pyromelliamide. The amide decomposed at 285 °C.

Pyromellitonitrile (60)

A stirred suspension of 2 g (0.08 mol) pyromellitamide in 12 mL DMF was warmed to 60 °C before 3.84 g (0.032 mol) thionyl chloride was added dropwise. After the mixture was heated for 7 h at 60 °C, dilute hydrochloride acid was added to decompose unreacted thionyl chloride, and the mixture was filtered. The residue was washed with water until it was neutral to litmus and then was slurried four times in hot, glacial acetic acid and filtered hot. After cooling in a refrigerator overnight, it was filtered and a tan solid was obtained. Recrystallization from ethanol. Yield: 0.67 g (47.26 percent); m.p.: 264 to 267 °C (same as literature); IR: 2,245(CN); 3,113, 3,048 (CH); 916(1,2,4,5-substitute) cm-1.

Preparation of the Bis-1,3-diiminoisoindoline (61)

A rapid stream of gaseous ammonia is bubbled through a solution of 2 g (0.01 mol) pyromellitonitrile (60) and 0.6 g sodium methoxide in 40 mL absolute methanol at room temperature for 1 h. The solution is heated at reflux for a further 4 h, while the addition of ammonia is continued. The precipitate formed at the end is collected by suction and washed with small amounts of cold methanol; yield: 2.4 g (100 percent) light green-colored solid; m.p. > 300 °C. IR (KBr): 3,358 (N-H); 1,639 (C-N); 1,560 (C-N) cm-1.

Binuclear Phthalocyanine (51a) and Mononuclear Phthalocyanine (37)

1.5 g (2.9 mol) of compound 4 and 0.026 g (0.12 mol) of 7 were heated at 150 °C (oil bath) in 8 mL 2-N,N-dimethylaminoethan oil for 70 h under an argon atmosphere. The mixture gradually changed color from light green to dark green. After cooling to room temperature, the mixture was diluted with acetone, and the green-colored residue was filtered. The residue was subsequently extracted in a soxhlet apparatus with acetone (24 h), methanol (48 h), and ether (24 h). The product was further purified by flash chromatography using a 5- by 12-cm column. The green product was preadsorbed on silica and eluted with toluene to give monomeric 2,3,9,10,16,17,23,24-octakis(dodecyloxy)phthalocyanine compound 37 as a blue-green solid after solvent evaporation. Further elution with 2-methoxyethanol/ toluene (3/40) yielded a mixture of binuclear and mononuclear fraction after solvent evaporation. This fraction was further purified by gel permeation chromatography using a 3-cm wide column packed SX1 BioBeads 70-cm high. The mononuclear-binuclear fraction was eluted with freshly distilled toluene. The faster-moving band, consisting of binuclear species, was further purified by flash chromatography using toluene/2-methoxyethanol (40/3) as eluent and gave 40-mg dark-green binuclear 51a (10 percent), while the slower-moving band of mononuclear 37 species was not further purified. Analytical GPC column (THF as mobile phase) verified that binuclear 51a had less retention volume (i.e., higher molecular weight) than mononuclear Pc.

Binuclear 51a: IR:3,295(w, NH), 2,854/2,922(str,CH),1,607(NH),1,278(ArO),1,104(ArOC); 1H NMR 0.92–2.11(br. CH3(CH2)10-),4.58 (br,OCH2),8.2(br, aromatic); UV/VIS(CHC13) Xmax/nm[log E/dm3mol-1cm-1]:702(5.14),667(5.07).

Mononuclear 37: IR: 3,276(w,NH), 2,850//2,921(str,CH),1,611 (NH), 1,277(ArO),1,101(ArOC), 746;1H NMR:–2.5 to –2.9(br.,2H, NH),0.93–2.15(br, 184H,CH3(CH2)10-),4.50(br.,16H,OCH2),8.46 (br,s,8H,ArH);UV/VIS(CHC13) Xmax/nm[log E/dm3mol-1cm-1]:702(5.03),665(4.94, 646(sh),603(4.27).

Synthesis Bis-diimionisoindoline, 67 From 2,3,6,7-etracyanonaphthalene, 66

A rapid stream of gaseous ammonia is bubbled through a solution of 0.1 g (0.87 mol) 2,3,6,7-tetracyanonaphthalene and 17 mg sodium in 9 mL dry methanol/dioxane (1/1) mixture at room temperature for 1 h. The solution is heated with stirring at 80 °C for a further 2 h, while the addition of ammonia is continued. The brown-colored material was obtained after vacuum pull-out solvent, and the material was washed with small amounts of cold methanol. Yield:0.104g (90 percent) brown-colored solid; m.p. > 300 °C; IR(KBr):3,333(N-H); 1,638(C-N); 1,542(C-N) cm-1.

Binuclear Phthalocyanine (52a)

The crude diiminoisoindolines obtained from 18 mg (0.079 mol) 2,3,3,7-tetracyanonaphthalene and 1.0 g (1.9 mol) 1,3-bisimino-5,6-didodecyloxyisoindoline were heated at 150 °C (oil bath) in 7 mL 2-N,N-dimethylaminoethanol for 70 h under an argon atmosphere. The mixture gradually changed color from light green to dark green. After cooling to room temperature, the mixture was diluted with acetone, and the green-colored residue was filtered. The residue was subsequently extracted in a soxhlet apparatus with acetone (24 h), methanol (48 h), and ether (24 h). The produce was further purified by flash chromatography using a 3- by 12-cm column. The green product was preadsorbed on silica and eluted with toluene to give monomeric 2,3,9,10,16,17,23,24-octakis (dodecyloxy)phthalocyanine as a blue-green solid after solvent evaporation. Further elution with 2-methoxyethanol/toluene (3/40) yielded after solvent evaporation a mix of binuclear and mononuclear fraction. This fraction was further purified by gel permeation chromatography sing a 3-cm wide column packed with SX1 BioBeades 70-cm high. the mononuclear-binuclear fraction was eluted with freshly distilled toluene. The faster moving band consisting of binuclear species was further purified by flash chromatography using toluene/2-methoxyethanol (40/3) as eluent and gave 15-mg dark-green binuclear Pc(0) (6 percent), while the slower moving band of mononuclear species was not further purified. The analytical GPC column (THF as mobile phase) verified that binuclear Pc(0) had less retention volume (i.e., higher molecular weight) than mononuclear Pc.

Binuclear Pc(0): IR: 3,197(w, NH), 2,854/s,923 (str,CH), 1,603(NH), 1,278 (ArO), 1,096(ArOC); 1H NMR 0.92–2.11(br. CH3(CH2)10-), 4.58(br,OCH2); UV/VIS(CHC13) Xmax/nm[log E/dm3mol-1cm,-1]: 720(4.55), 694(4.62).

Tetraphenyl-o-phthalonitrile (46)

A solution of 12.8-g (0.33-mol) tetraphenylcyclopentadienone, 44, and 2.8-g (0.036-mol) furmarnitrile, 45, in 24 mL of bromobenzene was refluxed for 2 h. The reaction mixture was allowed to cool and then 8-g (0.05-mol) of bromine in 8.5 mL bromobenzene was slowly added down and followed by refluxing for 3 h. Cooling gave a crop of crystals which was filtered and was washed with 7 mL of cold toluene and the 7 mL of cold petroleum ether (b.p. 90 to 100 °C). The residue was recrystallized three times from toluene and three times from benzene to a constant melting point, affording colorless crystals. Yield: 4.0 g (28 percent); m.p.:265 °C(literature:265.3–265.4 °C), IR: 2,227(CN);3,057 (CH).

1,3-Diimino-4,5,6,7-tetraphenyl-isoindoline, 47

A rapid stream of gaseous ammonia is bubbled through a solution of 2-g (4.60 mol) tetraphenyl-o-phthalonitrile and 0.4-g sodium in 50 mL absolute methanol and 50 mL dioxane at room temperature for 1 h. The solution is heated with stirring at reflux for a further 4 h, while the addition of ammonia is continued. The yellow-colored material was obtained after vacuum pull-out solvent, and the material was washed with small amounts of cold methanol; yield: 1.7 g (72 percent) light-yellow colored solid; m.p. > 300 C. IR(KBr):3,325(N-H); 1,654(C-N); 1,577(C-N) cm-1.

1,2,3,4-Tetraphenyl-9,10,16,17,23,24-hexakis(dodecyloxyl)phthalocyanine, 48

0.5-g (1.1 mol) crude 1,3-diimino-4,5,6,7-tetraphenyl-isoindoline in 10 mL of N,N-dimethylaminoethanol was heated to 150 °C (oil bath) under an argon atmosphere. Compound 4, 0.57-g (1.1 mol), was then added over five portions within 5 h. The mixture was heated at 150°C for an additional 70 h under an argon atmosphere. The mixture was cooled to room temperature, diluted with acetone, filtered, and washed thoroughly with methanol until the filtrate was almost clear. The crude product was extracted with methanol in a soxhlet apparatus to remove yellow impurities. The desired product was then extracted 24 h with diethyl ether. The produce was further purified by flash chromatography using 2-methyloxyethanol/toluene (3/40) given as a green solid. Through H NMR aromatic region integration ratio, it showed that it was mainly mono-tetraphenyl substitute Pc with some di-tetraphenyl substitution Pc. Yield: 0.20 g (28 percent based on mono-tetrasubstitute Pc). IR: 3,316 (NH); 2,853/2,922(str,CH);1,105(ArOC)cm-1. HNMR: 0.93–2.3 (m,br,CH3(CH2)10);4.32(s,OCH2); 7.18–7.64(m,4ArH-Pc);8.57–8.66(d,ArH). UV/VIS(CHC13) Xmax/nm:700,678,640(sh),615.

1,8-Dibromonoaphthalene, 31

A 2-liter, three-necked, round-bottom flash was charged with 26.7 g (0.167 mol) of 1,8-diaminonaphthalene and 333 mL of 6.9M sulfuric acid. The suspension was cooled to –20 °C before adding 34.0-g (0.493-mol) sodium nitrite and 225 mL of water followed by a solution of 38.6-g (0.269-mol) copper (1) bromide in 400 mL hydrobromic acid. This mixture was brought to room temperature before heating to 50 °C for 1 h followed by heating overnight at 40 °C. It was then heated for 3 h at 65 °C before cooling to 0 °C. At this temperature, solid sodium hydroxide was added until basic. The mixture was extracted using THF (tetrahydrofuran) and diethyl ether. It was treated several times with charcoal in hexane. Finally, it was crystallized three from dilute alchohol and animal charcoal [1] to give 1.31 g of 1,8-dibromonaphthalene (yield 2.6 percent), m.p. 106–108 °C; IR spectrum was identical to that published before reference 5.

1,8-Dicyanonaphthalene, 26

1.3-g (0.004-mol) dibromononaphthalene, 31, was added to 11 mL DMF (dimethylformamide) followed by bubbling through nitrogen for 20 min. Copper (1) cyanide (1.680-g, 0.0187-mol) was introduced and a nitrogen atmosphere was maintained. It was refluxed for 4.5 h. At first, it was bright yellow but became dark orange after 2.5 h. This mixture was added to 5.110 g sodium cyanide in 120 mL water. The resulting solution was extracted with 4/100 mL portions of methylene chloride until colorless. Concentration of the extract was carried out, and the crude 1,8-dicyanonaphthalene was crystallized from methylene chloride (fawn-colored needles), m.p. 231/232 °C. It was purified by sublimation and finally by recrystallization from alcohol (yield 75.2 percent) to give a light-green solid, m.p. 232/233 °C; IR(KBr, cm^{-1}): 2,240, 2,220 (CN). NMR (CDCL$_3$) 8.45–7.40 (m, aromatic H).

Preparation of 11

0.5400-g (2.8-mol) of 1,8-dicyanonaphthalene was added to 42 mL of sodium in 50 mL solvent (25 mL methanol, 25 mL dimethoxymethane). Ammonia was bubbled through for 1 h at room temperature. The temperature was increased to 80 °C for 3.5 h before a sample was taken, which showed no peak at 2,240 cm^{-1} or 2,220, and thin-layer chromatography indicated the absence of starting material.

Diethyl ether was used as an eluent, but was unable to separate the product from the other materials, so we tried chloroform and got very good separation. The reaction mixture was stored overnight in the freezer under nitrogen to increase crystallization, but ended up pulling a vacuum to remove the solvents. It was passed through an alumina column after adding acetic acid and the fractions were collected. They were washed with water and methanol to remove the acetic acid. Further column chromatography was necessary with methanol as the solvent. Separation was achieved. Yield: m.p.; IR(cm^{-1}): 3,500–3,290(w), 2,922(s), 2,870(w), 1,568(s), 1,460(m); ^{1}HNMR: 8.54–8.59 (d,aromatic H), 8.27–8.40 (t,aromatic H), and 7.64–7.84 (t,aromatic H).

CONCLUSIONS

The project has seen a number of significant milestones reached. The first is the successful synthesis of a new bisphthalocyanine based upon a naphthalene core. The second milestone was the synthesis of the key 1,8-naphthalene intermediate compound 11. This compound is the key to a new and unique class of phthalocyanine. Compound 11 is the first example of its type and the first amine/imine tautomer to be isolated. The proton and carbon thirteen NMR's illustrate that this compound does not tautomerize rapidly on an NMR time scale, as had been proposed previously in the literature.

The isolation of a green, stable new compound based upon compound 11 is the first of its type to be synthesized. It represents a new series of chemicals which may possess unique catalytic, conductivity, or photochemical properties.

The work on these structures represents several breakthroughs and firsts. The integral use of molecular modeling, including quantum mechanics with synthesis, has proven that the combination is the best approach to technological advancement of this area. We have found barriers, stable targets, and interpeted results which would not have been possible without molecular modeling or without the synthetic results.

The future of this area is very bright. The new class of compounds containing one 1,8-naphthalene system must be expanded and further evaluated. The electrochemistry of systems containing the naphthalene core must be explored to evaluate electron transfer communication differences between it and the benzene core system.

The photochemical degradation inhibition of plastic by phthalocyanine compounds has been studied. Instead of undergoing photodegradation under UV exposure, the polymer undergoes photo-polymization and crosslinking with an absence of oxygen. DD green behaved similarly to blue on the UV protection for the plastic. Both pigments decreased the photopolymerization process of polystyrene. Further work will be required to understand the mechanism of this photopolymerization process.

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APPROVAL

NEW DIRECTIONS IN PHTHALOCYANINE PIGMENTS
(Center Director's Discretionary Fund Final Report No. 90-25)

By Diep Vo Trinh

The information in this report has been reviewed for technical content. Review of any information concerning Department of Defense or nuclear energy activities or programs has been made by the MSFC Security Classification Officer. This report, in its entirety, has been determined to be unclassified.

Paul H. Schuerer

P.H. SCHUERER
Director, Materials and Processes Laboratory

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Phthalocyanines have been used as a pigment in coatings and related applications for many years. These pigments are some of the most stable organic pigments known. The phthalo blue and green pigments have been shown to be ultraviolet (UV) stable and thermally stable to over 400 °C. These phthalocyanines are both a semiconductor and photoconductor, exhibiting catalytic activity and photostabilization capability of polymers. Many metal free and metallic phthalocyanine derivatives have been prepared. Development of the new classes of phthalocyanine pigment could be used as coating on NASA spacecraft material such as glass to decrease the optical degradation from UV light, the outside of the space station modules for UV protection and coating on solar cells to increase lifetime and efficiency.

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