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A novel unsymmetrical metal-free phthalocyanine with a nitro group as an acceptor substituent and three *t*-butyl groups as donor groups, namely nitro-tri-*t*-butylphthalocyanine (NtBuPc) was synthesized for the first time by mixed condensation of two corresponding diiminoisoindolines. The NtBuPc can be separated by common column chromatography on silica gel using chloroform-hexane as the elution solvent. The structure was confirmed by elemental analysis, nmr, uv-vis, ir and mass spectroscopy. No contamination of either symmetrical or other related phthalocyanines was observed.

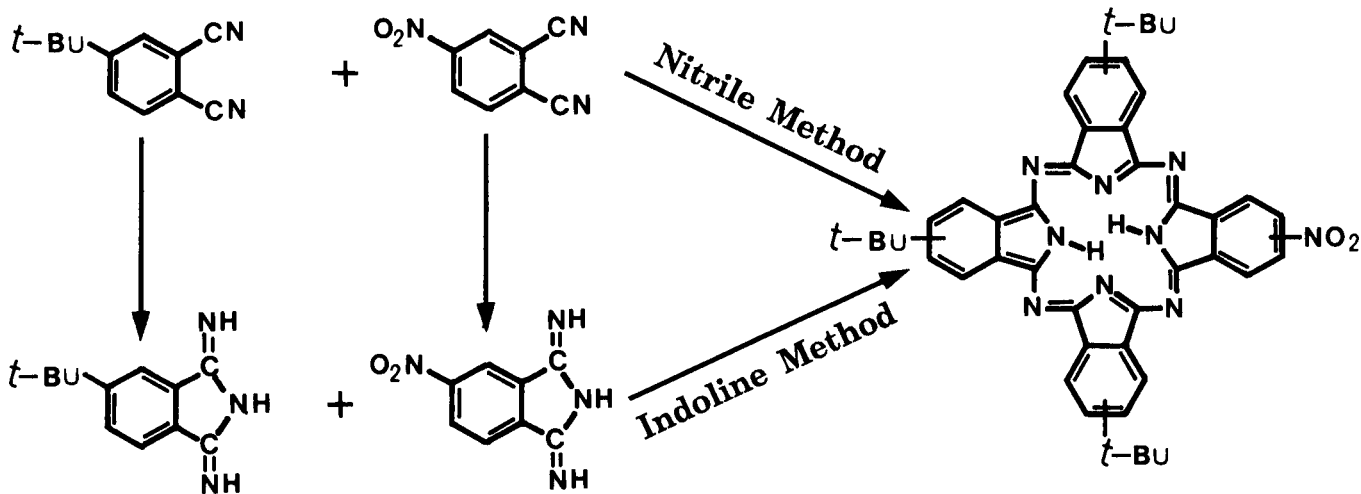
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Introduction.

Unsymmetrical substituted phthalocyanines have attracted much interest in recent years not only because of their outstanding electronic and optical properties but also their versatility of fabricating into a thin film by the Langmuir-Blodgett (LB) technique. Although many efforts have been made to synthesize an unsymmetrical phthalocyanine, its synthesis still remains a difficult problem both in preparation and in purification. Several strategies have been tried in the literature. The simplest one is through a mixed condensation of two different substituted 1,3-diiminoisoindolines, but statistical mixtures of compounds, likely inseparable by common column chromatography, would be bound to occur [1]. Hence, the number of the

substituent was usually a decimal number which was suggested by elemental analysis rather than a whole number [2,3]. The other one is that the substituted diiminoisoindolines were attached to an insoluble polymer and reacted with a large excess of a second diiminoisoindoline in solution, then an unsymmetric substituted phthalocyanine could be formed, and subsequently liberated from the polymer [4]. Obviously, this method is rather complicated. Leznoff and co-workers developed another approach by using a crossed condensation of a diiminoisoindoline and a dithiophthalimide, but selective formation of mono- or disubstituted phthalocyanines was only partially achieved [5]. We are interested in a phthalocyanine derivative with donor-acceptor substituents substituted at one phthalocyanine

Scheme 1. Synthesis of NtBuPc.



cyanine molecule [6]. Recently, we succeeded in the synthesis of such an unsymmetrical phthalocyanine with a nitro group as an acceptor substituent and three *t*-butyl groups as donor substituents, namely nitro-tri-*t*-butylphthalocyanine (NtBuPc). In this paper, its synthesis and characterization was reported.

EXPERIMENTAL

All chemicals were of reagent grade. All solvents were dried over molecular sieves (4 Å) and distilled before use. Infrared (ir) spectra were recorded on a Perkin-Elmer 683 infrared spectrophotometer. Nuclear magnetic resonance (nmr) spectra for protons were recorded on a JNM-FX 100 spectrometer using deuteriochloroform as the solvent and the CHCl₃-proton remained in the deuteriochloroform as the internal standard ($\delta = 7.25$ ppm). Ultraviolet-visible (uv-vis) were recorded on a Hitachi 340 spectrometer. Mass spectra (ms) were recorded on a Finigan Mat 90 mass spectrometer in the FD mode.

5-*t*-Butyl-1,3-diiminoisoindoline (**1**) and 5-Nitro-1,3-diiminoisoindoline (**2**).

Compound **1** was prepared as previously described [7]. In the case of compound **2**, a significant modification was made as follows: A solution of 4-nitrophthalonitrile (5.0 g, 28.9 mmoles) in 75 ml of a mixture of dry methanol-dioxane (2:1) was stirred at room temperature with a vigorous flow of ammonia gas bubbling through for 2 hours. It was then heated to reflux while ammonia gas was continuously introduced for an additional 5 hours. After cooling, the mixture was concentrated below 40° under reduced pressure until the volume was reduced to 100 ml. The crystals produced were filtered, washed with dry methanol and dried *in vacuo*.

These crude isoindolines were used directly in the condensation reaction without further purification. Nitrile absorption in their ir spectra was not observed.

Nitro-tri-*t*-butylphthalocyanine (**3**).

A mixture of 3.02 g (15 mmoles) of **1** and 0.95 g (5 mmoles) of **2** in 25 ml of *N,N*-dimethylaminoethanol (DMAE) was heated under reflux and stirred under an argon atmosphere for 7 hours. After cooling to room temperature, the mixture was poured into 500 ml of methanol and allowed to stand overnight. The precipitate was filtered with suction followed by washing with methanol. The crude product was separated by column chromatography on silica gel (10-40 μ) using chloroform as the eluent to yield two bands. The first band was collected and applied to column chromatography again using a mixture of chloroform-hexane (2:1) as the eluting solvent to give two portions. They were tetra-*t*-butylphthalocyanine and NtBuPc, respectively. The second band was also purified by column chromatography once again using chloroform as the eluting solvent. For this band, the mass spectrum indicated that they were still a mixture of related phthalocyanines. Further effort to purify and identify the products were necessary. All of these products were extracted with methanol in a Soxhlet extractor for 6 hours and then dried *in vacuo* at 160° for 5 hours.

Results and Discussion.

Nitrile Method.

Substituted phthalocyanines usually can be synthesized either by high temperature melt condensation using phthalonitriles as the reactant (nitrile method) or by low temperature solution condensation using diiminoisoindolines as the reactant (indoline method). In the case of the nitrile method, phthalocyanine ring formation requires 2 electrons from a redox reaction in addition to the 16 π -electrons from the 8 nitrile groups to yield 18 π -electron aromatic system [8]. A classical Lindsey preparation of metal-free phthalocyanine from phthalonitrile proceeds through a dilithium phthalocyanine intermediate followed by proton-lithium ion exchange [9]. On the other hand, nucleophilic reagents that undergo a facile reduction to aromatic products such as 1,2,3,6-tetrahydropyridine (**3**), hydroquinone (**4**), piperidine, piperazine and thiazolidine are also a source of hydrogen for the conversion of phthalonitrile to metal-free phthalocyanines.

The nitrile method was used in the beginning in the hope to provide unsymmetrical phthalocyanines. A mixture of 4-*t*-butylphthalonitrile (BPN) and 4-nitrophthalonitrile (NPN) with either lithium, or sodium/**3/4** was reacted in a sealed tube with a Teflon-coated stirring bar as shown in Scheme 1. The reaction conditions are listed in Table 1.

Table 1
Preparation of NtBuPc via the Nitrile Method

No.	Feed (mmoles)			Conditions		Products
	BPN	NPN	Li/Na 3/4	Temp (°C)	Time hours	
1	6	2	Li	250	20	NtBuPc, BuPc
2	6	2	Na	250	15	NtBuPc, BuPc
3	6	2	3	250	20	BuPc
4	6	2	4	250	20	BuPc

These crude products were treated according to the procedures described in the literature [8]. For reactions 1 and 2, pieces of un-reacted lithium or sodium were observed while the glass tubes were broken. After purification by column chromatography, beside tetra-*t*-butylphthalocyanine (BuPc) a small amount of NtBuPc (yield ca. 0.3%) was obtained. However, for reactions 3 and 4, separation led only to the discovery of symmetrical BuPc and tris(4-*t*-butyl)-1,3,5-triazine as revealed by ir spectra [8] and no NtBuPc was formed.

Indoline Method.

The first step in the realization of the synthesis of NtBuPc (Scheme 1) is the preparation of the required 5-nitro-1,3-diiminoisoindoline (**2**). Indeed, the preparation of substituted diiminoisoindolines were known in our previously work [7] and in the literature [10,11]. The corresponding phthalonitrile was dissolved in dry methanol, then about 1/100 equivalent amount of sodium methoxide as a catalyst was added. The mixture was refluxed while a rapid stream of ammonia gas was bubbled into the mixture. Unfortunately, 4-nitrophthalonitrile is insoluble in methanol, therefore treatment of 4-nitrophthalonitrile with ammonia gas in methanol did not convert **2**. Later on we overcame this problem by using mixed solvent of methanol-dioxane (2:1). In addition, the catalyst of sodium methoxide was omitted since it is known that 4-nitrophthalonitrile can be nucleophilic substituted

by methanol to form 4-methoxyphthalonitrile under strongly basic conditions. The reason for such modification is to avoid this side reaction.

Statistical analysis shows that the mixed condensation of two types of diiminoisoindolines would give five products despite their isomers, *i.e.* BuPc, NtBuPc, dinitrodi-*t*-butylphthalocyanine (dNBuPc), tri-nitro-*t*-butylphthalocyanine (tNBuPc) and tetranitrophthalocyanine (NPc). If the feed ratio of **1** to **2** is 3, the theoretical yields can be calculated as 32% (C_{3n}^4/C_{4n}^4 , $n = \text{mole} \times 6.023 \times 10^{23}$), 42% ($C_{3n}^3 \cdot C_n^1/C_{4n}^4$), 21% ($C_{3n}^2 \cdot C_n^2/C_{4n}^4$), 4.7% ($C_{3n}^1 \cdot C_n^3/C_{4n}^4$) and 0.39% (C_n^4/C_{4n}^4), respectively.

In our separation system, silica gel as the parking material and chloroform-hexane as the eluting solvent, the R_f numbers for dNBuPc, tNBuPc and NPc are too small to move. These products may be adsorbed on the top of the column. Only BuPc and NtBuPc can be obtained in the yields of 4.6% and 7.3% respectively. Although the experimental yield of NtBuPc (7.3%) is lower than that of theory (42%), from practical point of view we are satisfied with the results.

Separation and Purification.

Due to the high solubility for the substituted phthalocyanines, most of them can be purified by methods normally applied to organic compounds, such as extraction with an organic solvent, precipitation in water or methanol, column chromatography on alumina or on silica gel using normal, flash [12], or vacuum methods [13], recrystallization, thin-layer chromatography (tlc), high performance liquid chromatography (hplc), sublimation and followed by drying *in vacuo* at high temperatures. However, all phthalocyanines exhibit strong aggregation effects. Their π -electronic interaction for dimerization is comparable in strength to hydrogen bond formation, as indicated by a dimerization enthalpy of -14 kcal/mole [14]. Phthalocyanines also interact and form weak complexes with solvents, particularly those with π -electron systems. It often happens that bands, eluting from a column or spots on tlc that supposedly represent a pure substituted phthalocyanine, can incorporate unsubstituted phthalocyanine or other phthalocyanines [5]. Therefore, although the products were purified in some cases the compounds gave unacceptable elemental analyses and the mass spectral data revealed that they are a mixture of phthalocyanines. We investigated various purification methods in detail and found the combination procedures of precipitating in methanol — column chromatography (at least twice) extraction with methanol — drying *in vacuo* at high temperatures can afford pure desired phthalocyanine products. Precipitation of the reaction product in methanol removed most non-phthalocyanine impurities. In the case of column chromatography on silica gel, we tried several eluting solvent systems, for example, benzene-ester, chloroform-hexane, xylene, *etc.*, to test the separating efficiency. The mixed solvent of chloroform-hexane (2:1) provided the best separation results. Our attempts at using column chromatography on alumina to separate this phthalocyanine mixture have not been successful. Extraction with methanol to remove minor impurities and drying *in vacuo* at high temperatures can remove adsorbed solvents.

Characterization.

Elemental analysis calcd. for $C_{44}H_{41}N_9O_2$: C, 72.60; H, 5.68; N, 17.32. Found: C, 72.51; H, 5.74; N, 17.10.

Highly conjugated molecules such as porphyrins, phthalocyan-

ines as well as the recently discovered new fullerenes often give unacceptable elemental analyses because of their π -electronic interaction and the adsorbed solvents. In our hands, our product had the following elemental analytical data.

Anal. Calcd. for $C_{44}H_{41}N_9O_2$: C, 72.60; H, 5.68; N, 17.32. Found: C, 72.51; H, 5.74; N, 17.10.

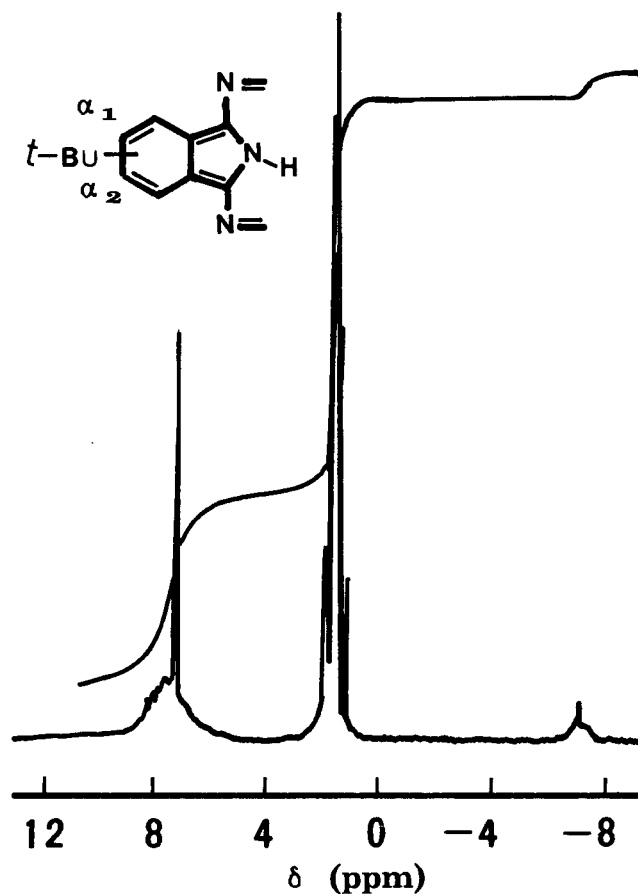


Figure 1. The ¹H nmr spectrum of NtBuPc in deuteriochloroform.

Figure 1 shows the ¹H nmr spectrum of NtBuPc in deuteriochloroform. The chemical shifts of the *t*-butyl protons, the aromatic protons and the cavity protons of NtBuPc are at 1.65, 8.50~6.50 and -7.14 ppm, respectively. The signal at -7.14 ppm is a characteristic of the inner N-H broad absorption peak. The *t*-butyl groups and the nitro group can either locate at the α₁ or the α₂ position on the benzene ring (see the insert of Figure 1). This generates four geometric isomers and eight magnetically non-equivalent protons for NtBuPc. The ¹H nmr signals at 8.50~6.50 ppm are broad due to a mixture of a large number of possible position isomers. From the nmr integration, the ratio of the number of cavity protons to the *t*-butyl protons for NtBuPc is 14, which is in reasonable agreement with the expected value calculated from its molecular formula (13.5). Because of the signal overlap of the chloroform-proton in deuteriochloroform and the aromatic proton, the number of the aromatic protons was difficult to estimate.

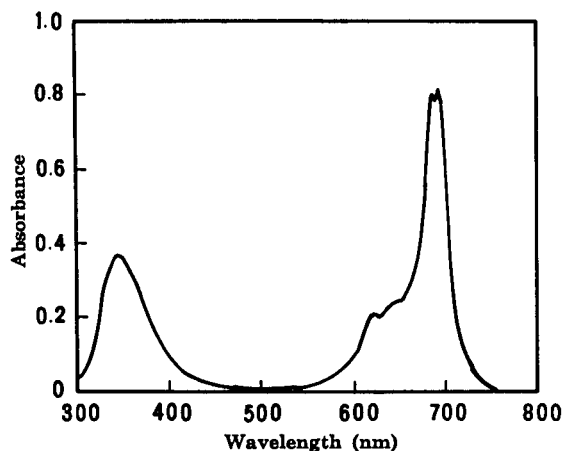


Figure 2. The uv-visible spectrum of NtBuPc in deuteriochloroform.

In Figure 2 is the electronic absorption spectrum of NtBuPc in chloroform. The metal-free phthalocyanines have a D_{2h} symmetry and shows a doublet at 691 nm and 683 nm together with a weaker band at 621 nm. The band in the region 615-700 nm is the Q band, while the band in the region 350-400 nm marks the B band envelope. Between them there is a "window" region, which is very useful for the second harmonic generation research [6]. The absorption spectrum is most affected by aggregation processes. Phthalocyanine derivatives are well known to aggregate in solution. In all cases, aggregation leads to a significant shift in the maximum of absorption in the visible region and to a broadening of the peaks. The narrow longer wavelength absorption has been attributed to a monomeric phthalocyanine compound and the partially resolved broad adsorption from 60 to 70 nm shorter wavelength has been attributed to a dimer complex [15-17].

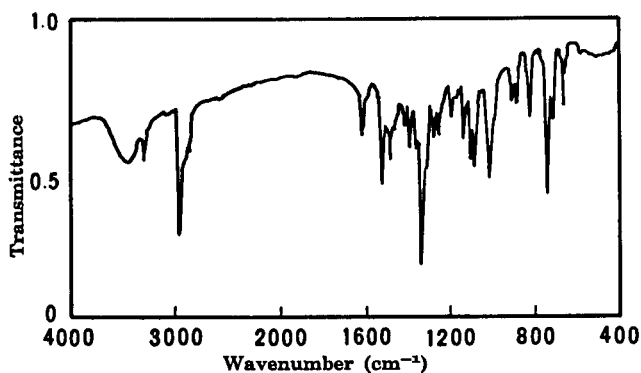


Figure 3. The ir spectrum of NtBuPc.

Figure 3 depicts the ir spectrum of NtBuPc. The ir bands characteristic of the metal-free phthalocyanine ring are a ring vibration at 1010 cm^{-1} and an N-H stretching band at 3290 cm^{-1} . The ir spectrum confirmed the presence of the nitro group (1520 and 1340 cm^{-1}) attributed respectively to the asymmetric and symmetric stretching modes of the nitro group [18].

The compositions of NtBuPc was subjected to mass spectral analysis. An intense parent ion ($m/z = 728$, 100%, $M^+ + 1$) was observed as shown in Figure 4. The most interesting feature of

the mass spectrum is in the region of 500-1300, only one m/z value was observed, demonstrating the high purity of NtBuPc.

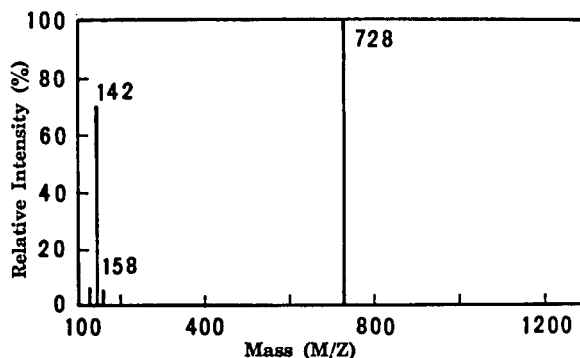


Figure 4. The mass spectrum of NtBuPc.

Conclusions.

Nitro-tri-*t*-butylphthalocyanine was synthesized by mixed condensation for the first time. In the case of the indoline method the yield was as high as 7.3% while it was very low *via* the nitrile method. NtBuPc could be separated and purified by the combination procedures commonly used for organic compounds.

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