Synthesis of 1,2,3,4-Tetraphenyl-9,10,16,17, 23,24-hexadodecyloxyphthalocyanine

Jiang Yang, Thomas C. Rogers and Michael R. Van De Mark*

Department of Chemistry, University of Missouri-Rolla,
Rolla, Missouri 65401

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The unsymmetrical 1,2,3,4-tetraphenyl-9,10,16,17,23,24-hexadodecyloxyphthalocyanine was synthesized utilizing steric hinderance of a tetraphenyl group to limit substitution.

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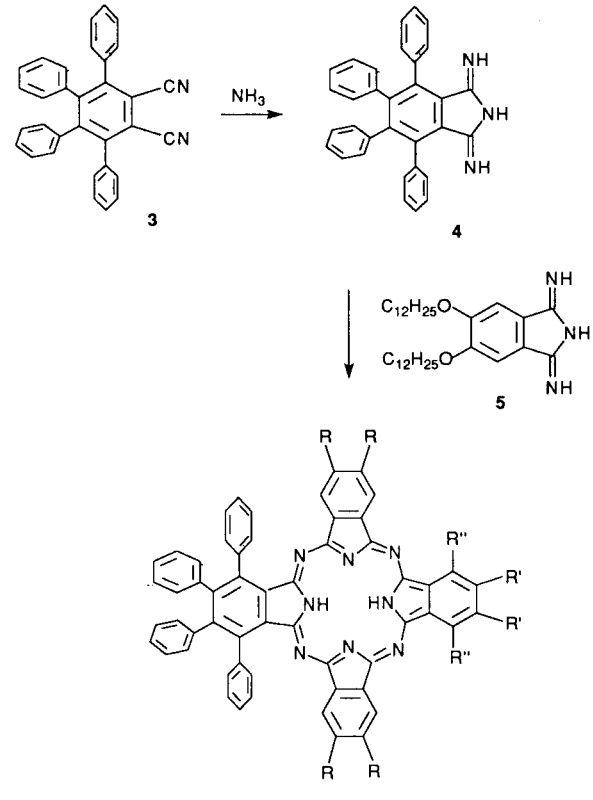
Although symmetrical tetra-, octa-, and hexadecasubstituted phthalocyanines are well known, the synthesis of simple mono [1], disubstituted [2] as well as other unsymmetrical phthalocyanines [3,4] remain a difficult problem. These compounds are important in understanding the nature and applications of phthalocyanines. For example, fine tuning of the position of the absorption band of phthalocyanine can be achieved by stepwise introduction of peripheral substituent groups [5]. Phthalocyanines are cyclic tetramers usually formed from a single phthalo monomer, AAAA, with the first being connected to the fourth mer. When cophthalates are used, mixed phthalocyanines are possible AAAB, BBBA, AABB and ABAB. The primary strategy to form unsymmetrical phthalocyanines such as AAAB or ABAB in past studies has been the mixed condensation of two different *ortho*-dinitriles of aromatic compounds or 1,3-diminoisoindolines. This approach gave mixtures of all possible combinations of the two phthalo monomers as phthalocyanines [4]. We here report the preparation of an AAAB system incorporating three didodecyloxy phthalo units and one tetraphenyl phthalo with minimal formation of the other cophthalates found in the past approaches.

Originally, molecular modeling using SYBYL and our experiments showed that the tetraphenyl substituted diminoisoindoline derivative **4** could not condense with each other to form the 1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-hexadecylphenyl phthalocyanine due to the steric hinderance of the phenyl groups. Therefore, we envisioned that only single **1a** AAAB and dual **2a** ABAB incorporation of the tetraphenyl segment into the opposite positions can form. No two units can be adjacent and coplanar due to steric hinderance. In order to purify and characterize the phthalocyanines, soluble systems were designed. Compounds **1b** and **2b** were therefore targeted.

The synthetic route to produce compound **1b** is summarized in Scheme 1. The tetraphenylphthalonitrile (**3**) was obtained by the condensation of the tetraphenylcyclopentadienone with furmaronitrile and subsequent dehydrogenation of the intermediately formed the product [6]. Compound **3** was then treated with ammonia [7] in the presence of sodium methoxide in methanol/dioxane (1/1) to give the diiminoisoindoline derivative **4** in 82% yield. Didodecycloxy substituted 1,3-diminoisoindoline derivative **5** was obtained from 1,2-dicyano-4,5-bis(dodecyloxy)-benzene [8] in quantitative yield using ammonia/sodium methoxide in dry methanol. Conversion of **4** from its *o*-dicyano of compound **3** was not quantitative, the steric hindrance of the tetraphenyl group may slow the nucleophilic subsitution of ammonia and allow other side reactions to occur.

Scheme 1



1a: R=R'=R''=H

1b: R=R'=$OC_{12}H_{25}$, R''=H

2a: R'=R''=  , R=H

2b: R'=R''=, R=$OC_{12}H_{25}$

A mixed condensation of **4** and **5** (1/3 molar ratio) in 2-*N,N*-dimethylaminoethanol at 150° for 70 hours gave, after purification, 1,2,3,4-tetraphenyl-9,10,16,17,23,24-hexa(dodecyloxy)phthalocyanine (**1b**) in 23% yield. In a similar experiment as above using mixed condensation of **4** and **5** in 1/1 molar ratio in an effort to synthesize 1,2,3,4,15,16,17,18-octaphenyl-9,10,23,24-tetradodecyloxyphthalocyanine, ABAB type, **2b** gave only single tetraphenyl substituted phthalocyanine, AAAB type in 25% yield, **1b** only without isolatable amount of **2b**. Due to the steric hinderance of the tetraphenyl substituents, the rate of incorporation of this unit into the system may be so slow as to preclude the formation of **2b** at a 1:1 ratio. It should be noted that in both reactions to form **1b** and **2b**, substantial amount of the AAAA system, 2,3,9,10,16,17,23,24-octakis-(dodecyloxy)phthalocyanine, formed as expected.

The infrared spectrum of compound **1b** showed the characteristic phthalocyanine NH absorption band at 3316 and 1024 cm^{-1}. The visible/ultra-violet spectrum of **1b** differed from 2,3,9,10,16,17,23,24-octakis(dodecyloxy)-phthalocyanine [8]. The metal free phthalocyanine **1b** show the expected splitting of Q band at 678 and 700 nm. However the split is only 22 nm as compared to 38 nm of the 2,3,9,10,16,17,23,24-octakis(dodecyloxy)phthalocyanine at 665 and 703 nm. This narrower split of the Q band may be due to a change in the symmetry due to the incorporation of tetraphenyl group in **1b** and thus causes perturbation of the energy level. The phenyl substituents are at approximately a 45° angle to the phthalocyanine ring. The steric bulk on both faces of the phthalocyanine ring would reduce dimer formation in solution and also modify the electronic coupling of the two rings. Further studies as to the magnitude and solvent effects on the coupling are under way. It should be noted that electronically the phenyl groups should not significantly modify the system due to the 45° dihedral angle making the overlap of the π systems very low.

The proton nmr of **1b** was as expected, the multiple peaks st 7.18-7.64 δ region indicate presence of tetraphenyl group in phthalocyanine product, and ^1H nmr also shows the typical strong shielding of the cavity hydrogens at -2.1 δ.

In conclusion, the first tetraphenyl single substituted unsymmetrical phthalocyanine was synthesized, and the splitting of Q band was observed to be narrowed. The introduction of bulky phenyl groups on one ring changed some of the spectral properties of phthalocyanine in part as a result of the weakening of intermolecular interaction.

EXPERIMENTAL

Melting points were determined using a Fisher-Johns melting apparatus. The ir spectra were recorded on a Perkin-Elmer 1750 FT-IR spectrophotometer in potassium bromide pellets. The nmr spectra were recorded on a JEOL FX-100 Multinuclear NMR using TMS as the internal standard in deuteriochloroform. The uv/vis spectra were recorded on a Hitachi 2000 spectrometer. Flash chromatography was performed using silica gel of particle size 40-63 μm. Elemental analyses were performed by Galbraith Laboratories, INC, Knoxville, TN. Compound **3** was prepared according to reference [6]. 1,2-Dicyano-4,5-bis(dodecyloxy)benzene was also prepared in two steps from *o*-xylene according to reference [8].

1,3-Dimino-4,5,6,7-tetraphenylisoindoline (**4**).

A rapid steam of gaseous ammonia was bubbled through a solution of 2 g (4.6 mmoles) tetraphenyl-*o*-phthalonitrile (**3**) and 0.4 g of sodium in 50 ml of absolute methanol and 50 ml of dioxane at room temperature for 1 hour. The solution was then heated with stirring at reflux for 4 hours while the addition of ammonia was continued. The yellow colored material was obtained after removal of the solvent by distillation under vacuum. The material was washed with small amounts of cold methanol to yield 1.7 g (82%) light yellow colored solid, mp $>300°$; ir ν 3325 (NH), 1654 (CN), 1577 (CN) cm^{-1}; ^1H nmr: δ 6.84-7.24 (m, Ar).

1,3-Dimino-5,6-bis(dodecyloxy)isoindoline (**5**).

A rapid stream of gaseous ammonia was bubbled through a solution of 5 g (0.01 mole) of 1,2-dicyano-4,5-bis(dodecyloxy)benzene and 50 mg of sodium methoxide in 50 ml of absolute methanol at room temperature for 1 hour. The solution was then heated at reflux for 4 hours while the addition of ammonia was continued. At the end of addition, a precipitate formed which was collected by suction and washed with small amounts of cold methanol to yield 5.1 g (98%), mp 125° dec with green color; ir: ν 3215 (NH), 1602 (CN), 1553 (CN), 1039 (ArOC) cm^{-1}.

1,2,3,4-Tetraphenyl-9,10,16,17,23,24-hexadodecyloxy Metal Free Phthalocyanine (**1b**).

Compound **4**, 0.2 g (0.44 mmole) and 0.68 g (1.33 mmoles) of 1,3-diimino-5,6-bis(dodecyloxy)isoindoline (**5**) in 4 ml of 2-*N,N*-dimethylaminoethanol was heated at 150° (oil bath) under an argon atmosphere for 70 hours. The mixture was then 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 **1b** was then extracted with diethyl ether for 24 hours while the 2,3,9,10,16,17,23,24-octakis(didodecyloxy)phthalocyanine which was formed by self condensation of **5** was left in the thimble. The product was further purified by flash chromatography using 2-methyloxyethanol/toluene (3/40, v/v) which gave 0.19 g (23%) green solid **1b**. The product was still contaminated with trace 2,3,9,10,16,17,23,24-octakis(didodecyloxy)phthalocyanine and was passed through a gel permeation column using Bio-beads SX1 (Bio-rad) with toluene eluent to purify it further; ir: ν 3316 (NH), 2853/2922 (CH), 1105 (ArOC), 1024 cm^{-1}; ^1H nmr: δ -2.1 (br, 2H, NH), 0.93-2.3 (br, 138H, $C_{11}H_{23}$-), 4.32 (s, 12H, $-CH_2O$), 7.18-7.64 (m, 22H, aromatic), 8.57-8.66 (br, 4H, aromatic); uv/vis (chloroform): λ max/nm[log ϵ/$dm^3mol^{-1}cm^{-1}$] 700 (5.01), 678 (4.97), 640 (sh), 615 (4.34).

Anal. Calcd. for $C_{128}H_{178}N_8O_6$: C, 79.86; H, 9.33; N, 5.82; O, 4.99. Found: C, 79.70; H, 9.21; N, 5.92; O, 5.17.

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