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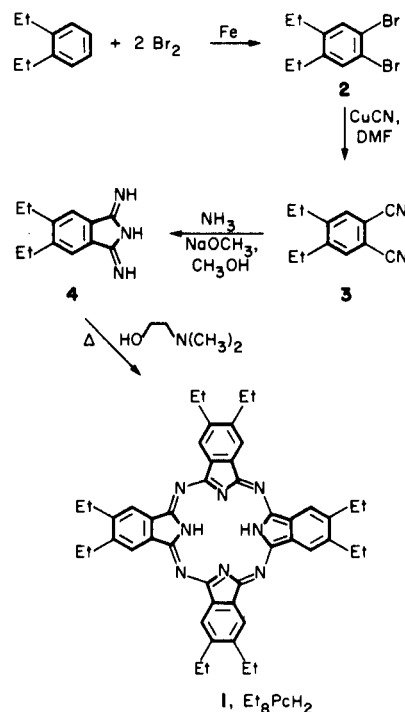
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The first preparation of 2,3,9,10,16,17,23,24-octaethylphthalocyanine (**1**) and synthetic precursor molecules is described.

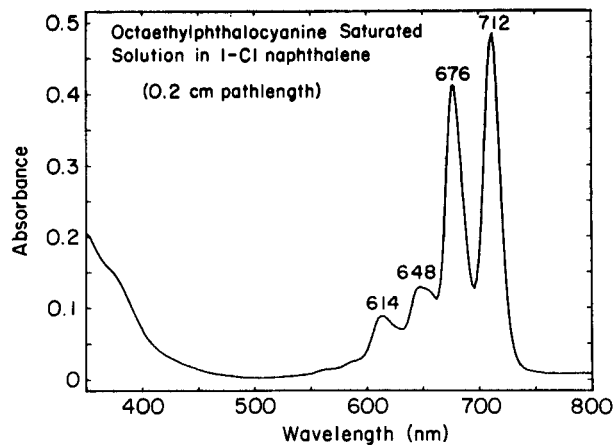
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The study of the solution chemistry of phthalocyanines and metallophthalocyanine complexes has been limited by the low solubility of these species in most organic solvents [1,2]. The complexes of the related porphyrin macrocycle are also very insoluble, but complexes of octaethylporphyrin have good solubility properties and have been extensively investigated [3]. In the interest of generating highly symmetric and soluble phthalocyanines and metallophthalocyanines we explored the possibility of preparing 2,3,9,10,16,17,23,24-octaethylphthalocyanine (**1**) from readily available precursors. While this work was in progress, the synthesis of the related octamethyl- and octabutylphthalocyanine complexes were reported, and those heterocyclic compounds were found to exhibit very low solubilities in chlorinated aromatic solvents [4]. Recently the synthesis of octa(alkoxymethylene)phthalocyanines was reported by Pawlowski and Hanack. These species also had low solubilities in organic solvents [5]. We report here the first synthesis of octaethylphthalocyanine (**1**) and its synthetic precursors using chemistry similar to that of Pawlowski and Hanack (Scheme and Experimental).

The mass spectral analysis and analytical data indicate that the product, heterocycle **1** is isolated in high purity. Saturated solutions of the compound in most organic solvents gave only faintly colored solutions. Assuming that the extinction coefficient for the ~ 712 nm band in **1** is the same as in octabutylphthalocyanine ($\epsilon = 184,000$ at 708 nm in 1,2,4-trichlorobenzene) [4], the approximate solubility of **1** in a variety of solvents can be calculated from the visible spectra in saturated solutions. Samples of **1** (~ 2 mg) were heated in 2 ml of each solvent typically to give slightly colored solutions. When cooled, the color in the solutions diminished due to reprecipitation of the compound. The solutions were let stand for at least 24 hours to allow equilibrium to be approached before the visible spectra were determined. The solubilities determined spectrophotometrically are upper limits since the solutions may still be supersaturated. At $\sim 25^\circ$, **1** is insoluble (*i.e.* the concentration is $\ll 1 \mu\text{M}$) in the following solvents: toluene, *N,N*-dimethylformamide, *N,N*-dimethylacetam-



ide, dimethylsulfoxide, acetic acid, nitrobenzene, chlorobenzene, pyridine, and chloroform. The upper limits of the solubility of **1** in 1-chloronaphthalene, 1,2,4-trichloro-



benzene, and quinoline are 13 μM , 8.5 μM , and 6 μM respectively. The visible spectrum of **1** in 1-Cl-naphthalene is given in the figure below. The heterocyclic compound dissolves readily in concentrated sulfuric acid to give brown solutions. The important conclusions of this study is that the solubility of **1** in organic solvents is very low, $\sim 10 \mu\text{M}$ at best. In light of the low solubility of **1** and the reported low solubility of even the octabutylphthalocyanine complexes [4], the solution redox chemistry and catalysis of octaalkylphthalocyanine complexes will not likely prove as promising as that of the corresponding more soluble octaalkylporphyrin complexes.

EXPERIMENTAL

Synthesis of 1,2-Dibromo-4,5-diethylbenzene (**2**).

A 100 ml 3-neck flask was equipped with an addition funnel, thermometer, and nitrogen source. Powdered iron (0.7 g, 12.5 mmoles) and 32.9 (245 mmoles) of 1,2-diethylbenzene were added and cooled to 0° under nitrogen. The reaction vessel was covered with aluminum foil to eliminate light, then 78.4 g (490 mmoles) of liquid bromine were added over a 4.5 hour period. The solution was stirred for an additional 4 hours while being allowed to warm slowly to 15°. The dark brown solution was filtered, washed twice with aqueous sodium bicarbonate, once with 0.1 N sodium thiosulfate and dried with magnesium sulfate. The solution was heated with activated carbon, filtered, then rapidly distilled *in vacuo* at a pressure of ~ 2 torr. The first 1 ml of distillate was discarded, and a second 65.8 g fraction boiling near 115° (at 2 torr) was collected. The distillate was cooled to -30° overnight to give large rectangular crystals of the product. These were separated and allowed to melt (mp $< -1^\circ$) to give 13.3 g of the product. The mother liquors were diluted with 40 ml of hexane and were cooled to -48° to give a second crop of crystals. The combined yield was 41.4 g (58%). The product was $> 95\%$ pure based on the nmr spectrum; ^1H nmr (deuteriochloroform): δ 1.3 (t, 3H), 2.65 (q, 2H), 7.4 (s, 1H).

Synthesis of 1,2-Dicyano-4,5-diethylbenzene (**3**).

A mixture of 20.4 g (0.07 mole) of 1,2-dibromo-4,5-diethylbenzene, 18.0 g (0.20 moles) of cuprous cyanide, and 250 ml of dimethylformamide was heated at reflux under nitrogen for 4.5 hours then allowed to cool. The reaction mixture was filtered, poured into 500 ml of concentrated aqueous ammonia, stirred for ten minutes, then extracted with 200 ml of benzene. The benzene layer was washed three times with concentrated aqueous ammonia and four times with water, dried with magnesium sulfate, then the benzene was removed *in vacuo* to give 11.9 g of white crystals contaminated with a brown impurity. The compound was purified by a bulb-to-bulb vacuum transfer to yield 10.7 g of a colorless solid. This solid was dissolved in 15 ml of hot toluene, diluted with 50 ml of hexane,

and cooled to 5° to yield 9.24 g (72%) of slightly green crystals. No impurities were detected in the spectrum; ^1H nmr (deuteriochloroform): δ 1.3 (t, 3H), 2.8 (q, 2H), 7.75 (s, 1H).

Synthesis of 5,6-Diethyl-1,3-diimino-1,3-dihydroisindole (**4**).

A flask containing 3.75 g (0.02 mole) of 1,2-dicyano-4,5-diethylbenzene (**3**) and 85 ml of anhydrous methanol was heated to 65° until the dinitrile dissolved, then gaseous ammonia was passed through the solution for 4 hours. Some precipitation occurred in the solution during this time. The green solution was cooled to room temperature and the precipitate was collected by filtration, rinsed with methanol, and air-dried to afford 3.24 g of slightly green crystals. Recrystallization from 75 ml of anhydrous methanol and drying *in vacuo* overnight yielded 2.34 g of white flakes (57%).

Anal. Calcd. for $\text{C}_{12}\text{H}_{15}\text{N}_3$: C, 71.61; H, 7.51; N, 20.88. Found: C, 71.57; H, 7.39; N, 20.80.

Synthesis of 2,3,9,10,16,17,23,24-octaethylphthalocyanine (**1**).

A mixture of 2.29 g (0.0114 mole) of 5,6-diethyl-1,3-diimino-1,3-dihydroisindole (**4**) and 22 ml of dimethylaminoethanol was refluxed for 7 hours and allowed to cool. The purple product was collected by filtration, rinsed with hexane, and air-dried to give 0.8 g of product. This solid was Soxhlet extracted for 2 days with pyridine and the pyridine solution was discarded. The unextracted material was dried *in vacuo* then Soxhlet extracted for 3 days with 200 ml of chlorobenzene. After cooling the chlorobenzene extract, the purple flakes of the product were collected by filtration, rinsed with hexane, and dried at 100° *in vacuo* to yield 0.48 g (23%) of pure **1**. The limited solubility of **1** precluded obtaining a good ^1H nmr spectrum for this material; ms: m/e (relative intensity) = 738 (M^+ , 100%), 369 (M^+ , 28%), 185 (7%). The remaining peaks between m/e 55 and 830 all had intensities $< 5.6\%$.

Anal. Calcd. for $\text{C}_{48}\text{H}_{50}\text{N}_6$: C, 78.02; H, 6.82; N, 15.16. Found: C, 77.98; H, 6.81; N, 15.42.

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