Synthesis and Vapor Spectrum of Zinc Tetrabenzporphine

Lawrence Edwards, Martin Gouterman,* and Charles B. Rose

Contribution from the Department of Chemistry, California State University, Northridge, California 91324, the Department of Chemistry, University of Washington, Seattle, Washington 98195, and the Department of Chemistry, University of Nevada, Reno, Nevada 89507. *Received April 16, 1976*

Abstract: The synthesis of zinc tetrabenzporphine is reviewed and its vapor-phase spectrum is reported. The molecule shows spectra in the region 200 nm $< \lambda <$ 500 nm that resembles porphyrin rather than phthalocyanine. Particularly notable is the sharp Soret band. Vapor spectra are obtained at temperatures between 540 and 585 °C. A heat of sublimation of $\Delta H = -32 \pm 3$ kcal/mol (-134 ± 13 kJ/mol) was found. Luminescence studies show persistence of a porphyrin-type impurity with Soret band at $\lambda \sim$460 nm and visible band $\lambda \sim$645 nm in spite of vigorous purification methods.

Introduction

Of the various porphyrins known, relatively little work has been published on the tetrabenzporphine (TBP) series. After several TBP's and TBP derivatives were first synthesized and their properties investigated,[1-4] the only work to appear concerning their chemistry was the investigations of Linstead and Weiss.[5] Some scattered spectroscopic work has been done on the TBP series. The fluorescence polarization spectra of the metal complexes show D_{4h} symmetry and the free base D_{2h}.[6-8] In Shpol'skii's experiments[9] in hydrocarbon snows at 77 K, MgTBP and ZnTBP were observed to show quasiline structure,[8] i.e., at low temperature the normally broad solution absorption bands resolve into sharp line multiplets, with the individual components having line widths of a few cm^{-1}.

Theoretical work on the electronic spectra of the TBP's using the Pariser-Parr-Pople method for π electrons has been reported.[10] As there had been no x-ray crystallography work on the TBP series, these calculations used the coordinates of NiPc.[11] The calculations predict strong visible absorption bands for TBP complexes, as are observed. More recently, iterative extended Hückel calculations have been done on TBP and phthalocyanine (Pc).[12] These calculations have clarified differences among the central proton structures of the free bases of TBP, Pc, and other porphyrins. They also explain the diffuseness of the Pc Soret bands (i.e., near uv bands) compared with the sharpness of the TBP Soret bands by the presence of n-π* bands underlying the Soret in Pc but not TBP, an explanation earlier proposed for similar diffuseness in other aza aromatic compounds.[13] This sharp Soret structure of TBP carries down to low temperatures, where quasiline structure has been reported for the ZnTBP Soret band.[14,15] The quasiline structure led to discovery of luminescence from the Soret band, so that ZnTBP is one of the few aromatic compounds to show three luminescences: $S_2 \rightarrow S_0$, $S_1 \rightarrow S_0$, and $T_1 \rightarrow S_0$.[14] The emission $S_2 \rightarrow S_0$ has also been found in CdTBP and H_2TBP, and its polarized fluorescence has been studied.[16]

In this paper we review the synthesis of ZnTBP and report its vapor spectrum. The latter allows careful comparison to the more recent theoretical calculations,[10b] in particular to high-energy absorption bands which are usually obscured by customary solvents such as pyridine.

Preparation of Zinc Tetrabenzporphine

ZnTBP (I) was prepared according to the general procedure of Linstead and Weiss.[5] This entails the use of a template reaction involving zinc acetate and isoindolinone-3-acetic acid (II) at elevated temperatures. The necessity for using such an unconventional and low-yield method is twofold. First, the so-called Rothemund reaction,[17] which provides one of the few simple methods for the preparation of reasonable amounts of porphyrins, would require the use of the highly unstable (indeed, not yet isolated) and only recently prepared isoindole (III)[18] as a precursor. Moreover, although porphyrin yields using the Rothemund procedure can be improved by the use of metal salts in the reaction[19] and many mechanistic studies have been carried out which carefully outline optimum conditions for this method,[20] yields are reasonable only where the porphyrins produced are substituted on the methine bridges by phenyl groups or their derivatives.

Metallic derivatives of TBP have been prepared by several other methods utilizing various precursors by several research groups. For example, Linstead's group obtained low yields of very impure ZnTBP when they treated *o*-cyanocinnamic acid with zinc salt at elevated temperatures.[3] Early in the synthetic studies of nonnaturally occurring tetrapyrrole pigments, Helberger and co-workers had prepared the metallic salts of both tetrabenzmonazaporphyrin[4a] (the tetrabenzporphyrin skeleton with a nitrogen atom replacing one of the methine CH groups) and tetrabenztriazaporphyrin[4b] using metal salts and acetophenone derivatives at high temperatures. He further accomplished the preparation of the metallo derivatives (including the iron, magnesium, and zinc salts) of the TBP by utilizing *o*-cyanoacetophenone,[4c] 3-methylphthalimidine,[4c] and numerous other phthalimidines (generally substituted in the 3 position) as well as phthalimidine itself.[4d] Finally a novel recent synthesis of the TBP system has been accomplished by Bonnett's group[21b] utilizing the pyrolysis of 1,3,4,7-tetramethylisoindole[21a] in an inert atmosphere with metal powders or salts, giving metallooctamethyltetrabenzoporphyrins. These methods, however, hold no advantages over the preparation employed in this study because yields are generally poorer, contaminants are difficult to remove, or the products were substituted tetrabenzporphine.

Our synthesis starts with the commercially available α-nitro-β-naphthol (IV). When IV is treated with *p*-toluenesulfonyl chloride and dilute aqueous base in acetone, ring opening occurs via a second-order Beckmann rearrangement[22,23] to give *o*-cyanoallocinnamic acid (V) in moderate yield. Then V may be smoothly converted to isoindolinone-3-acetic acid (II) in a high-yield Michael-type addition by treatment with hot aqueous alkali followed by acidification. Thus we have accomplished the conversion IV → V → II.

To prepare ZnTBP (I), II was mixed with an excess of zinc acetate dihydrate and ground into a fine powder. This mixture was heated under a nitrogen atmosphere for several hours in an electrical tube furnace, during which time a mixture of gases, including CO_2, H_2O, and CH_3CO_2H, was evolved. The dark violet reaction mixture was taken up in hot pyridine and the deep-green solution treated with dry ether to precipitate

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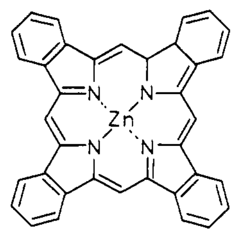
* Author to whom correspondence should be addressed at the University of Washington.



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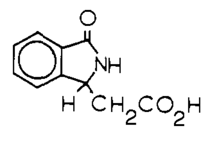

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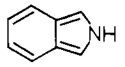

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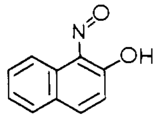

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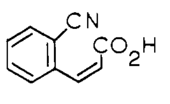

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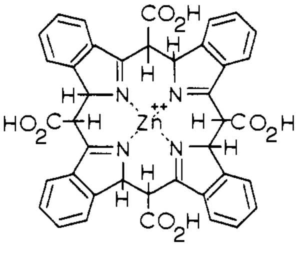

VI

inorganic salts and polymeric material. The solution was then concentrated and methanol added to precipitate the crude bright blue-purple ZnTBP. The material thus obtained is quite impure and must be subjected to elaborate purification, which is based on the extraordinary stability of ZnTBP to high temperatures.[24] Thus the ZnTBP is heated to 450 °C under N_2, which chars all nonporphyrin material. This is followed by repeated column chromatography, described below.

Although it is hazardous to predict the intermediates in this type of high-temperature, low-yield, "magic" cyclization, it may be useful to speculate on the more reasonable possibilities. In analogy with porphyrin condensations,[20b] one might envision four molecules of II condensing around Zn^{2+} with loss of four waters to give intermediate VI, which can then lead to I by loss of four molecules of CO_2, three molecules of H_2, and two protons.

Linstead,[3] in discussing the formation of the porphyrin ring, envisaged two stages: chain formation, followed by cyclization. He believed cyclization occurred to a dehydroporphyrin, followed by metal fixation. Although this latter proposal concerning metal fixation seems unlikely in view of more recent studies of the Rothemund reaction,[19,20] the bulk of his postulates are consistent with current knowledge of the mechanisms of porphyrin formation. When one considers the various possible reactions that could sidetrack macrocycle formation, the low yield is not surprising. Nonetheless, moderate amounts of pure pigment can be prepared by this process.

Experimental Section

All melting points (except as noted) were obtained using a Hershberg apparatus equipped with Anschütz thermometers and are corrected. NMR spectra at 60 MHz were recorded on a Varian Associates A-60 spectrometer using tetramethylsilane as an internal standard with the specified solvents. Infrared spectra were measured on a Perkin-Elmer Model 137 spectrophotometer. Visible spectra were measured on an Applied Physics Corporation Cary 14 recording spectrophotometer. Mass spectra were recorded on an Associated Electrical Industries MS-9 double-focusing mass spectrometer using perfluorokerosene as an internal standard for exact mass determinations and a direct inlet system heated to 350 °C.

o-Cyanoallocinnamic Acid (V). A modification of Edwards[25] procedure was employed. A solution consisting of 17.3 g (0.100 mol) of α-nitroso-β-naphthol[26] (IV) and 20.0 g (0.105 mol) of p-toluenesulfonyl chloride in 80 ml of acetone was prepared at 55 °C. To this mixture, immersed in an ice/water cooling bath, 10% aqueous NaOH was added dropwise at such a rate to maintain a temperature of 55–60 °C. When the solution became permanently basic its temperature dropped, and the mixture was cooled and vacuum filtered through a pad of Filter-cel. The resulting solution was diluted slightly with water, and the acetone was removed in vacuo and acidified with concentrated hydrochloric acid with cooling. The tan precipitate was collected by vacuum filtration, washed with cold water, and subsequently recrystallized from 400 ml of water using charcoal and vacuum filtration through Filter-cel. Generally on recrystallization at this stage a black tarry residue was encountered on dissolution of the product. This residue did not appear to be soluble in hot water and was easily removed by the Filter-cel. Slow cooling of the filtrate yielded 8.50 g (0.049 mol; 49.0%) of long, pale golden needles: mp 137–139 °C (lit.[25,27] mp 137 °C); ir spectrum (KBr) 2230 (C≡N), 1700 (C=O), 1630 (C=C), and 1600 cm^{-1} (aromatic); NMR spectrum ($CDCl_3$) δ 6.2 (1 H, doublet, C*H*CO$_2$H, J = 12.5 cps), 7.3 (1 H, doublet, Ar-CH, J = 12.5 cps), 7.6 (4 H, multiplet, aromatic H), and 10.6 ppm (1 H, singlet, CO$_2$M).

Isoindolinone-3-acetic acid (II). V was cyclized in aqueous base following the general procedure of Rowe, Haigh, and Peters.[28] V (8.66 g, 50.0 mmol) was dissolved in 50 ml of 10% aqueous sodium hydroxide, and the resulting mixture was refluxed for 3 h. The warm reaction mixture was transferred into a beaker, and concentrated hydrochloric acid was added dropwise with magnetic stirring, and a finely divided colorless precipitate was obtained. After the mixture was cooled, the product was collected by vacuum filtration and air dried. This crude product after recrystallization once from 150 ml of water using activated charcoal gave colorless prismatic needles (8.69 g, 45.5 mmol, 91%): mp 181–182.5 °C (lit.[28] 182 °C); ir spectrum (KBr) 3430 (sharp, NH), 2500–2950 (CO$_2$H), 1710 (C=O, acid), 1650 (C=O, lactam), and 1620 cm^{-1} (aromatic); NMR spectrum (($CD_3)_2SO$) δ 2.8 (2 H, unsymmetrical ABX septet, C*H*$_2$CO$_2$H$^-$), 5.0 (1 H, overlapped ABX doublets, >C*H*CH$_2$), 7.7 (4 H, multiplet, aromatic H), 8.7 (1 H, singlet, CO$_2$H), and 12.4 ppm (1 H, broad singlet, >NH). The spectrum suggests the existence of an internally bonded structure of zwitterionic nature involving the acetic acid proton and the indolinone nitrogen free electron pair.

Zinc Tetrabenzporphyrin (I). A finely divided mixture of **II** (3.5 g, 18.3 mmol) and zinc acetate dihydrate (2.6 g, 11.8 mmol; J. T. Baker) was prepared by prolonged grinding of the two with a mortar and pestle. This mixture was then placed into a 3 × 25 cm Pyrex reaction vessel containing a ST 34/45 joint and fitted with gas inlet and exit tubes, and a slow stream of dry nitrogen was passed through the tube while it was placed into a tube furnace at 350 °C for 3.5 h. At the end of this time the tube was withdrawn from the furnace and cooled. During the reaction, the outlet for nitrogen flow from the tube must be vented to a hood as a dense white vapor carrying a strong odor of acetic acid is emitted. The cooled tube contained a deep-violet colored solid melt. The melts of two identical reactions were combined and treated with several portions of hot reagent grade pyridine yielding a deep Kelly-green solution (combined volume was 150 ml). This was cooled and poured into 500 ml of reagent diethyl ether, and the resulting mixture was vacuum filtered, the volume reduced in vacuo, and 100 ml of reagent methyl alcohol added. After cooling, the resulting deep-purple plates of crude zinc tetrabenzporphyrin amounted to 1.60 g (2.8 mmol, 30.5%).

I was purified as follows. The above product (1.60 g) was placed in one side of a 12 × 50 cm Pyrex tube containing a fritted glass plate fused in the middle. This tube and its contents were then heated between 400 and 455 °C for one-half of an hour under a slow stream of dry nitrogen. The tube was cooled, and a slight amount of oily liquid on the opposite side of the glass frit from the sample was removed with a swab dampened with pyridine. **I** was then removed by dissolution in hot reagent pyridine and passing it through the fritted disc under nitrogen pressure leaving behind an insoluble carbonaceous residue. The resulting deep-green solution was then chromatographed first on a 2 × 35 cm column of 60/100 mesh Florisil[29] using pyridine as

Table I. Absorption Data

	T, °C	λ, nm	$\bar{\nu}$, cm^{-1}	$\Delta\lambda_{1/2}$, nm	$\Delta\bar{\nu}_{1/2}$, cm^{-1}	λ (1 − 0) (nm)
Q band						
Vapor	583	625	16 000	35	890	580
Pyridine	25	628	15 950	12	300	581
B band						
Vapor	539	405	24 690	23	1400	
Pyridine	25	433	23 095	10	530	

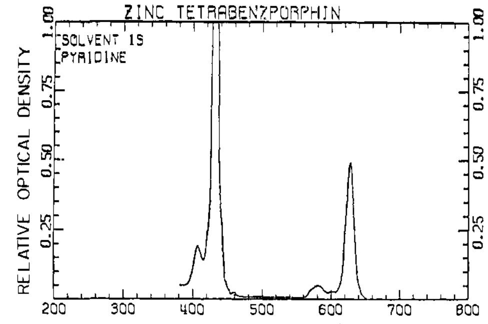

Figure 1. Absorption spectrum (relative optical density) of ZnTBP in pyridine. See Experimental Section for molar extinction coefficients.

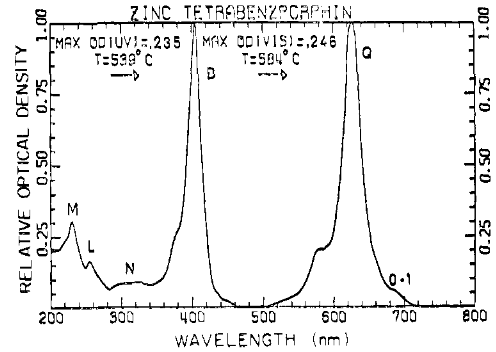

Figure 2. Vapor spectrum (relative optical density) of ZnTBP. Temperatures are shown. Maximum OD corrected to 1-cm pathlength.

Table II. Vapor Pressure[a]

T, °C	P, Torr
539	0.14
500	0.05
400	2×10^{-3}
300	4×10^{-5}

[a] ΔH is −32 ± 3 kcal/mol (−134 kJ/mol) determined as in ref 34.

Table III. Transitions of ZnTBP

	Theoretical[a]		Experimental	
State	E, cm^{-1}	f_2	E, cm^{-1}	f
Q	15 000	0.06	16 000	0.17[b]
B	26 000	0.94	24 700	0.92[b]
N	37 000	0.24[c]	31 200	~.3
L	42 000	0.08[c]	39 400	≳.2
M	48 000	0.50[c]	43 400	~.1

[a] Theoretical values from ref 10b. [b] From Linstead's data. [c] Sum of two neighboring bands.

eluent, followed by concentration and a second chromatograph on a 1 × 20 cm column of Woelm[30] aluminum oxide, also employing pyridine as the eluent. The volume was reduced in vacuo to about 10 ml, 100 ml of reagent methyl alcohol was added, and the mixture was cooled at 0 °C. It was then vacuum filtered and the collected material washed with methyl alcohol and dried first in air then under 5×10^{-2} Torr for 3 h. The yield of pure ZnTBP was 233 mg (14.5% recovery). An additional 58 mg was obtained from further workup of the chromatographic fractions.

The ZnTBP obtained from this purification process exists as bright-purple platelets with a metallic sheen and is insoluble in the common organic solvents (even when warm); solubility is best in pyridine with slight solubility being observed in hot dimethyl sulfoxide and hot α-chloronaphthalene. The substance does not melt[31] below 360 °C. The ir spectrum (KBr), although complex, is consistent with the accepted structure: 3000 (C–H weak), 1500–1700 (aromatic nucleus), and 695, 740, and 755 cm^{-1} (strong, aromatic deformations). Visible spectrum $\lambda_{max}^{pyridine}$ 628 (161 500), 602 (10 000), 582 (17 000), [460 (7500/ρ), where ρ is molar ratio of impurity to ZnTBP], 432 (502 000), and 408 nm (59 200). High-resolution mass spectrum ($C_{36}H_{20}N_4Zn$) M^+ calculated: 572.0970. Found: 572.0992.

Spectroscopic Results

The apparatus and technique used for the vapor study has been described elsewhere.[32] Figure 1 shows a solution spectrum of ZnTBP. An interesting feature is the rather clear peak at 460 nm, a peak also reported by Linstead. Luminescence excitation data show this peak is an impurity that gives a strong red fluorescence at 647 nm. Thus the impurity is a porphyrin-like material with Soret and visible bands to the red of ZnTBP. This impurity has survived the vigorous purification treatment described above as well as chromatography and sublimation. The nature of this exceedingly stable and similar contaminant is not clear. The spectra are not those expected for free-base TBP or another metallo TBP. One possibility is a hydrogenated compound with one or more benzene rings reduced.

Figure 2 shows the vapor spectrum of ZnTBP. The uv region has heretofore been unreported. A noticeable feature is that the spectrum for λ < 500 nm is much more like the vapor spectrum of porphyrin[32,33] than that of phthalocyanine.[34] In particular the Soret band is around 400 nm and is narrow like the porphyrin Soret band even though taken at considerably higher temperature. In contrast, the phthalocyanines show Soret bands around 335 nm and half-widths three times those of porphyrins and ZnTBP.

Table I summarizes the peaks observed for the spectra in pyridine and in vapor. Molar extinction coefficients for the pyridine spectra are given in the Experimental Section. Table II gives vapor pressure data and heat of sublimation. Table III gives a summary of the electronic bands and their oscillator strengths. The experimental oscillator strengths of the uv bands are accurate to only ±50% due to the breadth of the bands.

Discussion

Several features of our results should be emphasized. The vapor studies show again the great stability of the ring system. It is unfortunate that such a low-yield reaction must still be employed to make the ring. The optical spectra show that ZnTBP resembles porphyrin much more than phthalocyanine, and the uv spectra are in quite good agreement with theory.[10] The sharpness of the Soret band in vapor is unusual and undoubtedly is related to the fact that the low-temperature Soret band shows quasilines and that the Soret band fluoresces.[14] This must reflect a very small vibronic coupling between B and Q, which may stem from the large energy gap (8700 cm^{-1}) between them (Table I). Further study of the yields of the three emissions of this compound [$S_2 \rightarrow S_0$, $S_1 \rightarrow S_0$, and $T_1 \rightarrow S_0$] as a function of temperature and of variation in the molecular skeleton and in the central metal would throw a new light on radiationless decay processes.[16] Finally, the existence of an impurity with a Soret band at 460 nm and a fluorescence at 647 nm is very surprising. These peaks suggest a closely related compound, and determination of what this compound is may give insight into the peculiar stability of the TBP ring system.

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An Unusual Reversible Valence Bond Isomerization Hemi-Dewar Naphthalene to Naphthalene

Ira B. Goldberg,* H. R. Crowe, and Richard W. Franck

Contribution from the Science Center, Rockwell International,
Thousand Oaks, California 91360, and the Department of Chemistry,
Fordham University, The Bronx, New York 10458. *Received May 19, 1976*

Abstract: Evidence obtained by electron spin resonance indicates that 1,3,6,8-tetra-*tert*-butylnaphthalene and 1,3,8-tri-*tert*-butylnaphthalene isomerize through the dianion intermediate to form the corresponding hemi-Dewar naphthalenes. The isomerization reactions are facilitated through the nonplanarity of the parent naphthalene compounds. ESR spectra of the anion radical of the hemi-Dewar naphthalene anions are reported.

Introduction

The subject of valence bond isomerization has received a great deal of attention during the past several years.[1] In particular, the isomerization of benzene to Dewar benzene has been studied both theoretically and experimentally. Alkyl-substituted benzenes[2] as well as perfluoroalkyl-substituted[3] benzenes have been shown to yield Dewar benzene during continuous uv irradiation. It is still questioned whether the isomerization involves a singlet or triplet excited state.[4] Theoretical studies[5] suggest that the isomerization of benzenes occur through excitation of two electrons into the lowest un-