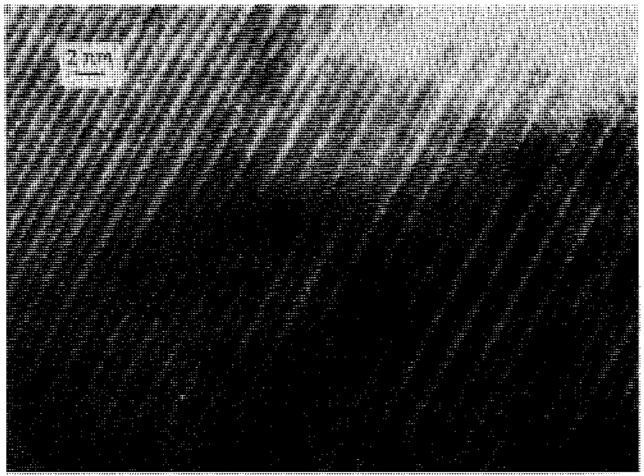

Figure 8. Lattice image of $BaIrO_3$ heated to 1400°C. This is somewhat similar to the image shown in Figure 3, but it has not been possible to analyze the detailed features of this image.

11.8, $b = 20.4$, and $c = 21.2$ Å. Lattice images of this high-temperature sample (Figure 8) were qualitatively similar to those of the 9H low-temperature phase but contained much more detail.

The reasons for the formation of the superstructure and for the *c*-axis contraction are not yet clear. However, we may note that 6H-$SrIrO_3$ has a monoclinic distortion of an orthorhombic supercell[14] based on $a \approx a_{hex}$ and $b = 3b_{hex}$. It is possible that the *c*-axis shortening may arise from some reduction of $BaIrO_3$ when it is heated to 1400°C. $SrIrO_3$ is known to undergo reduction in hydrogen below 400°C to give Sr_2IrO_4 together with Ir metal. While we do not have a clear explanation for the *c*-axis shortening or for the superstructure formation when $BaIrO_3$ is heated to 1400°C, the structural features found by us for the high-temperature phase provide an interesting comparison to those of the low-temperature 9H phase. It is possible that some of the weak reflections in the x-ray pattern of the low-temperature phase could arise from the presence of the high-temperature phase. However, more detailed studies of $BaIrO_3$ as a function of temperature would be necessary before we fully understand the transformations in the 1000–1400°C range.

Acknowledgment. The authors are grateful to Professor J. S. Anderson for the use of the electron microscope and for his interest in this work and to Professor B. L. Chamberland for providing a sample of 4H-$BaCrO_3$.

Registry No. $BaIrO_3$, 12230-76-1.

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Binding of Pyridine to Phenyl-Substituted Derivatives of Zinc Tetraphenylporphine

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Received July 28, 1975 AIC50542J

The binding of nitrogenous donors to metalloporphyrins has been studied in great detail.[2] Recently the adduct formation between zinc tetraphenylporphine and oxygen, sulfur, and phosphorus donors has been reported.[3] However, only a few studies have been reported in which the donor is held constant and the metalloporphyrin is changed gradually by varying the peripheral groups.[4] In this work the binding of pyridine to a series of *m*-phenyl- and *p*-phenyl-substituted derivatives of zinc tetraphenylporphine, Zn(*m*- or *p*-X)TPP, in the solvent benzene is reported.

Experimental Section

The phenyl-substituted tetraphenylporphines and the corresponding zinc porphyrins were synthesized by literature methods.[5,6] The zinc porphyrins were purified by dry-column chromatography.[3,6] Aldrich pyridine was purified as reported[7] and Baker Analyzed reagent benzene was treated as reported.[8] The absorbance measurements were made on a Cary Model 14 uv–visible spectrophotometer with a thermostated cell compartment. All measurements were made at 25° using quartz cells with 1-cm path length. All systems were studied at four different wavelengths and the spectral data for all the systems are listed in Table I available in the microfilm edition. The procedure for the treatment of the data has been reported.[3]

Results and Discussion

Table II contains the extinction coefficients of the phenyl-substituted zinc porphyrins prepared for this study, the substituent constants (σ_X), and log K where K is the equilibrium constant for the formation of the 1:1 adduct between pyridine and a zinc porphyrin. Figure 1 is a plot of log K vs $4\sigma_X$. Both the meta and para derivatives have been plotted on the same figure. In general, there is an increase in the binding of pyridine by the zinc porphyrin with increasing electron-withdrawing character of the substituent. Two metalloporphyrins deviate substantially from the least-squares line, ZnTPP and Zn(*m*-OCH_3)TPP. Examination of data from a recent study[4d] of the binding of piperidine to a series of *m*-phenyl- and *p*-phenyl-substituted derivatives of nickel tetraphenylporphine, Ni(*m*- or *p*-X)TPP, shows that the *m*-OCH_3 derivative for this system has a lower equilibrium constant toward piperidine than would be predicted from a least-squares line for the data of the other derivatives. A similar result is displayed in Figure 1. The determination of equilibrium constant for ZnTPP has been repeated several times and the results are the same within experimental error. Two other studies of the ZnTPP–py system have been reported[9,10] and data from these studies are presented in Table II and Figure 1.

The slope of the line in Figure 1 omitting the H and *m*-OCH_3 points is 0.188 ± 0.007. Similar plots for the VO(*p*-X)TPP–piperidine system and the Ni(*p*-X)TPP–piperidine[4d] system gave slopes of 0.113 ± 0.003 and 0.331 ± 0.005, respectively. Assuming no major differences occur in the mode of transmission of the electronic effects because of the different donors (pyridine vs. piperidine) and different solvents (benzene vs. toluene) used in this and the other study,[4d] it appears that the Zn(*m*- or *p*-X)TPP series is more sensitive to change on the periphery of the molecule than the VO(*p*-X)TPP series but less sensitive than the Ni(*p*-X)TPP series.

It has been suggested that the VO(*p*-X)TPP series is less sensitive to substituent changes than the Ni(*m*- or *p*-X)TPP

Table II

Metalloporphyrin	$10^{-4}\epsilon$ (550 nm)	σ_X[a]	log K
Zinc tetra(4-methoxyphenyl)porphine	2.52	−0.268	3.690 ± 0.002
Zinc tetra(4-methylphenyl)porphine	2.37	−0.170	3.721 ± 0.009
Zinc tetra(3-methylphenyl)porphine	2.48	−0.069	3.798 ± 0.032
Zinc tetraphenylporphine	2.30	0	3.724 ± 0.014 3.78 ± 0.02[b] 3.70[c]
Zinc tetra(4-fluorophenyl)porphine	2.13	0.062	3.907 ± 0.018
Zinc tetra(3-methoxyphenyl)porphine	2.30	0.115	3.844 ± 0.021
Zinc tetra(4-chlorophenyl)porphine	2.38	0.227	4.043 ± 0.025
Zinc tetra(3-fluorophenyl)porphine	1.98	0.337	4.087 ± 0.004
Zinc tetra(3-chlorophenyl)porphine	2.44	0.373	4.141 ± 0.005
Zinc tetra(3-bromophenyl)porphine	2.31	0.391	4.192 ± 0.005

[a] L. P. Hammett, "Physical Organic Chemistry", McGraw-Hill, New York, N.Y., 1970, p 356. [b] Data from ref 10. [c] Calculated from the data of ref 9.

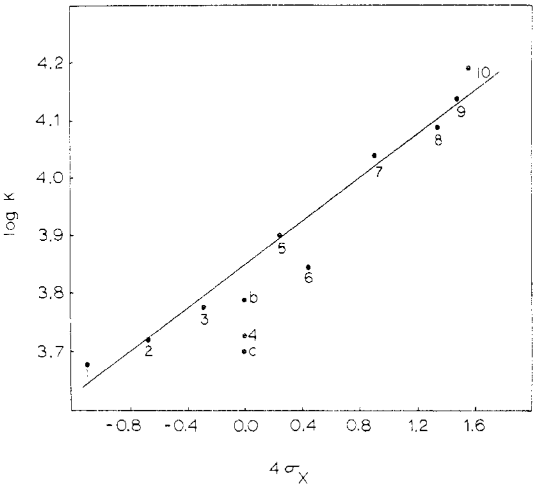

Figure 1. Plot of log *K* vs. σ_X: 1, *p*-OCH_3; 2, *p*-CH_3; 3, *m*-CH_3; 4, b, c, H; 5, *p*-F; 6, *m*-OCH_3; 7, *p*-Cl; 8, *m*-F; 9, *m*-Cl; 10, *m*-Br. See Table II.

series because metal to ligand π back-bonding is the more important means of electron delocalization in metalloporphyrins.[4d] The d orbitals of Zn(II) are completely filled and thus it is expected that the Zn(*m*- or *p*-X)TPP series will be more sensitive to change in peripheral groups than the VO(*p*-X)TPP series because the lone d electron is in the d_{xy} orbital in the case of V(IV)[11] and cannot interact with the π* system of the porphyrin ring.[4d] The work of Hoard and coworkers has shown that the Zn atom lies out of the plane of the porphine skeleton[12] and hence the d_π–L_{π^*} overlap may be considerably reduced in comparison to that of the Ni system. This reduced overlap may partially account for the Zn(*m*- or *p*-X)TPP series being less sensitive to change in peripheral groups than the Ni(*m*- or *p*-X)TPP series. Similarly, it has been found that zinc porphyins are less sensitive to substituent changes than the nickel porphyrins for the substituted 2,4-deuteroporphyrin system.[4a]

Acknowledgment. The authors wish to acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. Zn(*p*-OCH_3)TPP(py), 57304-76-4; Zn(*p*-CH_3)TPP(py), 57304-77-5; Zn(*m*-CH_3)TPP(py), 57304-78-6; ZnTPP(py), 24389-79-5; Zn(*p*-F)TPP(py), 57304-79-7; Zn(*m*-OCH_3)TPP(py), 57304-80-0; Zn(*p*-Cl)TPP(py), 57304-81-1; Zn(*m*-F)TPP(py), 57304-82-2; Zn(*m*-Cl)TPP(py), 57304-83-3; Zn(*m*-Br)TPP(py), 57304-84-4; Zn(3,5-di-OCH_3)TPP(py), 57304-85-5; Zn(3,4-di-Cl)TPP(py), 57379-35-8.

Supplementary Material Available: Table I containing the spectroscopic data for the zinc porphyrin–pyridine systems (4 pages). Ordering information is given on any current masthead page.

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Oxidation of Trimethylamine by Copper(II) Chloride[1]

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Received July 31, 1975 AIC505702

In previous studies[2-4] of the coordination and oxidation of aliphatic amines by copper(II) chloride, key steps in the complex reaction sequence were shown to be

$$\mathrm{CuCl_2 + e^- \rightarrow CuCl_2^- \rightleftharpoons CuCl + Cl^-}$$

$$\mathrm{RCH_2CH_2NR_1R_2 \rightarrow 2e^- + 2H^+ + \underset{\longrightarrow\ \text{polymer}}{RCH{=}CHNR_1R_2}}$$

Obviously, dehydrogenation of an alkyl to a (substituted) vinyl group would be impossible with only methyl substituents present, yet conversion of trimethylamine by warm copper(II) chloride to a dark tarry product, presumably by oxidation–reduction, had been observed.[5] Also, in their isobaric temperature–composition study of the copper(II) chloride–trimethylamine system, Simon and co-workers[6] observed the complexes to undergo irreversible thermal decomposition. Recent work by Kiesel and Schram[7,8] on the oxidation of trimethylamine by vanadium(IV) chloride, in which it was shown that the dimethylmethyleneammonium cation plays a key role as an intermediate amine oxidation product, prompted our further investigation of the trimethylamine–copper(II) chloride reaction.

Experimental Section

Materials and Technique These were as described previously.[2-4] Microanalyses were done by Galbraith Laboratories, Knoxville, Tenn.

Instrumentation. A Beckman IR8 spectrophotometer and an F&M 700 gas chromatograph were used. With the latter, fitted with 6-ft stainless steel columns packed with 5% tetraethylenepentamine on Fluoropak 80, authentic samples of mono-, di-, and trimethylamines eluted as a single unresolved sharp peak, cleanly separated from formaldehyde.