*J. Am. Chem. Soc.* **1987**, *109*, 2659–2668

# Synthesis, Spectroscopic, and Structural Studies of Extremely Short Chain Basket Handle Porphyrins and Their Zinc(II) Complexes

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**Abstract:** The synthesis of extremely short chain "basket handle" porphyrins is described. These molecules are derived from 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine bearing alkoxy chains (handles) of 4-, 5-, and 6-carbon atoms covalently attached at the *o*-phenyl positions. For the $n = 5$ and 6 free base porphyrins three different isomers are formed: cross-trans-linked (I), adjacent-trans-linked (II), and adjacent-cis-linked (III) isomers. For the butyl-bridged compound only the latter two could be obtained. Attempts to insert zinc(II) ion into the porphinato cores have been successful only for isomers II and III; isomer I could not be metalated. The structural assignment of the three different isomers is based on UV–vis and $^1$H NMR spectroscopy as well as on X-ray structure analysis of the Zn(II) complex of the hexyl-bridged isomer II. The Zn hexyl II complex crystallizes in the monoclinic system, space group $P2_1/n$, and cell dimensions at 296 K of $a = 8.608$ (2) Å, $b = 22.212$ (4) Å, $c = 13.774$ (2) Å, and $\beta = 91.90$ (1)° with two molecules per unit cell. The average Zn–N bond distance is 2.031 (3) Å with the zinc atom precisely centered in the porphinato plane. On the basis of the spectroscopic and preliminary structural data, it is shown that the porphyrin ring of isomer I is permanently distorted from planarity. Furthermore, from analysis of spectroscopic data for isomers II and III it appears likely that the porphyrin rings of the butyl-bridged compounds are also distorted significantly, while those of the pentyl- and hexyl-bridged porphyrins are planar.

Although the highly conjugated $\pi$-system of the porphyrin ring seems to dictate that the molecule should remain essentially planar, it has been suggested for some time that the porphyrin ring is fairly flexible. X-ray crystallographic data[1,2] have confirmed that porphyrin rings can be distorted by ruffling, doming, or even bending. Several authors have attributed specific importance of distortions to the properties of heme proteins, including the Perutz mechanism for the cooperativity of hemoglobin: Part of the movement of the proximal histidine has been ascribed to the existence of a domed porphyrin ring in the deoxy Hb state.[3] Changes from planarity may also affect the energies and electron density distribution of the $\pi$-orbitals.

In the last 10 years the design of synthetic metalloporphyrin model complexes has become a powerful method for probing structure–function relationships of hemeproteins.[4] To mimic some of the properties of the natural compounds so-called "picket-fence",[5] "pocket",[6] "capped",[7] "cyclophane",[8] "crowned",[9] "strapped",[10] "pyrrole-strapped",[11] "gyroscope-like",[12] and longer chain "basket handle"[13] porphyrins have been synthesized, but significant distortion of the porphyrin ring has been reported for only one of the "pyrrole-strapped" porphyrins synthesized by Dolphin.[11]

In an attempt to produce permanently distorted porphyrins and their zinc(II) analogues and to investigate their physical–chemical properties we have synthesized a series of so-called "basket handle" porphyrins shown in Figure 1. These compounds are derivatives of 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine (TPP), in which two opposite or two adjacent *meso*-phenyl ortho carbon atoms are bridged by an alkoxy chain (handle) with a varying number of carbon atoms, $n = 4$, 5, or 6. In comparison to the longer chain analogues synthesized by Momenteau and co-workers[13] we were able to introduce a strain in the porphyrin ring in some of our compounds due to the extreme shortness of the handles. We now report the synthesis of these compounds, which is based on a combination of Adler's,[14] Baldwin's,[15] and Momenteau's[13] synthetic routes to porphyrins, and their zinc(II) complexes as well as the results of UV–vis, $^1$H NMR, and X-ray structure investigations.

## Experimental Section

**NMR Spectroscopy.** One dimensional proton magnetic resonance spectra were recorded either on the General Electric GN-300 or QE-300 instruments at San Francisco State University, the Nicolet NT-360 instrument at the University of California, Davis, NMR facility, or a home-built BVX-300 or the Bruker AM 500 spectrometer at the University of California in Berkeley.

Phase sensitive homonuclear chemical shift correlated spectra (COSY,[16] TPPI method[17]) were taken of a 0.01 M solution of isomer

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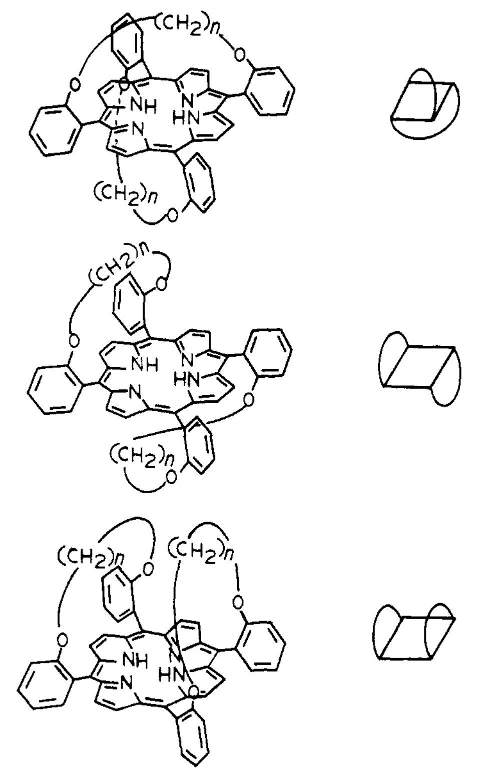

**Figure 1.** Sketches of the structures of the isomers I–III. Top: isomer I, obtained only for $n = 5$ and 6. Middle: isomer II, obtained for $n = 4$, 5, and 6. Bottom: isomer III, obtained for $n = 4$, 5, and 6.

II of the hexyl-bridged "basket handle" porphyrin in $CDCl_3$ and of saturated solutions of isomers II and III of the pentyl- and hexyl-bridged compounds in $CS_2$. The spectrum in $CDCl_3$ was recorded at the Chemistry Department of the University of California, Berkeley, on a home-built BVX-300 instrument equipped with a Nicolet 1280 computer and a Nicolet 293 A′ pulse programmer. Quadrature detection was used with a sweep width of 1449 Hz in $F_2$ and ±724.5 Hz in $F_1$. The size in $F_2$ was 512 w; 128 FID's were taken in $F_1$ with 16 scans each. The recycle delay was set to 1.2 s to give a total measuring time of 50 min. A nonshifted sine bell was used to process the two-dimensional dataset, and the phasing parameters were taken from the first FID with an initial delay to of 3 μs. The data were zerofilled twice in $F_1$ to give a final matrix of 512 w × 512 w with a corresponding digital resolution of 2.83 Hz/point. The COSY spectra in $CS_2$ were recorded on the GN-300 at San Francisco State University. Quadrature detection was used with a sweep width of 4184 Hz in $F_2$ and ±2092 Hz in $F_1$. The size in $F_2$ was 512 w; 256 FID's were taken in $F_1$ with 8 scans each, except for pentyl II, which required 64 scans each. The recycle delay was set to 1.0 s to give a total measuring time of 41 min (6 h for pentyl II). Processing of the COSY experiments was the same as above, except that one zero-filling was applied. Selective homonuclear decoupling experiments were taken at U. C. Berkeley on the AM 500 Bruker instrument equipped with an Aspect 3000 computer and a process controller.

**UV–vis Spectroscopy.** The electronic spectra, taken on a Perkin-Elmer 552 spectrophotometer and a Hewlett-Packard 8451A diode array spectrophotometer and recorded on a Hewlett Packard 7470A graphics plotter, were obtained at 22 ± 1 °C with use of 1.0 cm quartz cells, 0.9 cm quartz spacers, and a porphyrin concentration of $1 \times 10^{-4}$ M.

**Melting Points.** All melting points were recorded on a Hoover-Thomas melting point apparatus and are uncorrected.

**Materials.** All solvents and reagents not described were purchased either from Aldrich, E.M. Scientific, or J. T. Baker Co. Column chromatography was done on silica gel, 60–200 mesh, purchased from J. T. Baker Chemical Co. The thin-layer chromatography (TLC) was performed on commercially prepared Baker silica gel plates IB.

**General Procedure for the Syntheses of the Dialdehyde Derivatives.** Salicylaldehyde (0.24 mol, 25 mL) was added to an ethanolic solution of potassium hydroxide (1 M, 240 mL). A yellow precipitate, the potassium salt of salicylaldehyde, formed and then dissolved with refluxing. The appropriate dibromoalkyl derivative **1a**, **1b**, or **1c** (0.08 mol), depending on the desired dialdehyde product, was added dropwise. The solution was allowed to reflux for about 8 h and then cooled to below the boiling point. Filtration through a hot sintered glass funnel and slow cooling of the filtrate gave a pale yellow precipitate, which was recrystallized from ethanol, providing the corresponding colorless crystalline dialdehydes **2a**, **2b**, and **2c**. Butyl-bridged dialdehyde **2a**: yield 16.5 g = 69%; mp 84 °C; $^1H$ NMR ($CDCl_3$) δ (ppm) 10.49 (s, 2 H, CHO), 7.82 (dd, 2 H, *o*-phenyl H), 7.49 (t, 2 H, *p*-phenyl H), 7.02 ($m_c$, 4 H, *m,m′*-phenyl H), 4.18 (t, 4 H, *O*-$CH_2$), 2.10 (m, 4 H, β-$CH_2$). Pentyl-bridged dialdehyde **2b**: yield 19.7 g = 79%; mp 69.5 °C; $^1H$ NMR ($CDCl_3$) δ (ppm) 10.51 (s, 2 H, CHO), 7.83 (dd, 2 H, *o*-phenyl H), 7.49 (t, 2 H, *p*-phenyl H), 7.01 ($m_c$, 4 H, *m,m′*-phenyl H), 4.09 (t, 4 H, *O*-$CH_2$), 1.91 ($m_c$, 6 H, β,γ-$CH_2$). Hexyl-bridged dialdehyde **2c**: yield 22.2 g = 85%; mp 123.5 °C; $^1H$ NMR ($CDCl_3$) δ (ppm) 10.51 (s, 2 H, CHO), 7.82 (dd, 2 H, *o*-phenyl H), 7.53 (t, 2 H, *p*-phenyl H), 7.00 ($m_c$, 4 H, *m,m′*-phenyl H), 4.13 (t, 4 H, *O*-$CH_2$), 1.91 ($m_c$, 4 H, β-$CH_2$), 1.63 ($m_c$, 4 H, γ-$CH_2$).

**General Description of the Procedure for the Syntheses of the "Basket Handle" Porphyrins.** The desired dialdehyde **2a**, **2b**, or **2c** (0.03 mol) dissolved in 1200 mL of glacial acetic acid was put into a three-necked round-bottomed flask equipped with a magnetic stirrer, reflux condensor, dropping funnel, and air bubbler and heated to reflux. Pyrrole (0.065 mol) dissolved in 50 mL of glacial acetic acid was added dropwise. Air was bubbled through the solution, which turned from colorless to red to black. Total reflux time was 3 h. During the reflux the formation of the corresponding porphyrin products was followed by TLC and UV–vis spectroscopy. After the mixture was cooled, the black precipitate (probably polymerization products of pyrrole) was filtered off and discarded, and the filtrate was evaporated to dryness. The resulting black material was washed several times with portions of 50 mL of hot methanol to remove most of the black tar-like products. The remaining purplish powder was dissolved in a minimum amount of chloroform and loaded onto a 6 × 30 cm pressurized column of silica gel (Baker chromatographic grade, 60–200 mesh). After elution with chloroform, the hexyl- and pentyl-brigded "basket handle" porphyrins showed three spots on silica gel TLC plates with toluene as eluting solvent. They were identified as three different isomers as will be shown below. Except for the leading spot of the $n = 5$ compounds all spots fluoresced under long-wave UV radiation. TLC of the butyl-bridged ($n = 4$) compounds showed only two spots. After evaporation of the solvent the following product mixtures were obtained: "basket handle" porphyrin $n = 6$:mixture of three isomers, 750 mg = 5.9%; "basket handle" porphyrin $n = 5$:mixture of three isomers, 580 mg = 4.7%; "basket handle" porphyrin $n = 4$:mixture of two isomers, 725 mg = 6.2%.

**Separation of the "Basket Handle" Porphyrin Isomers.** The "basket handle" porphyrin isomer mixtures were dissolved in appropriate solvents or mixtures of solvents as described below and then put onto a 3 × 110 cm column and eluted with different solvent mixtures as noted in the following sections. The first porphyrin band coming down the column, the least polar compound, was identified by $^1H$ NMR spectroscopy and preliminary single X-ray crystal structure investigations as isomer I, the cross-trans-linked isomer. Bands II and III, collected separately, were attributed respectively to isomers II (adjacent-trans-linked isomer) and III (adjacent-cis-linked isomer). All fractions containing the isomers were evaporated to dryness and were treated by subsequent column chromatography until almost all tar-like products were removed. In the final purification step the residues were treated three times with activated charcoal either in toluene or in a mixture of toluene/ethyl acetate, followed by recrystallization each time to give purple crystals.

For the hexyl-bridged "basket handle" porphyrins, the three isomers were separated on a preparative silica gel column with hexane–toluene (1:3) as elution solvent and recrystallized from toluene with activated charcoal. The three isomers of the pentyl-bridged "basket handle" porphyrins were separated on a silica gel column with toluene–methylene chloride (1:1) as eluent and recrystallized from toluene with activated charcoal. Only isomers II and III of the butyl-bridged "basket handle" porphyrins were observed on a silica gel column (methylene chloride–ethyl acetate, 1:1). Also, refluxing the reactants in glacial acetic acid under nitrogen for 1 h, followed by a second hour of reflux under an oxygen atomsphere, did not produce isomer I in any detectable yield. The isomers were recrystallized in ethyl acetate with activated charcoal. The following yields were obtained for the short chain "basket handle" porphyrins: $n = 6$, I = 0.8%, II = 1.9%, III = 3.2%; $n = 5$, I = 0.2%, II = 2.9%, III = 1.6%; and $n = 4$, I = 0%, II = 3.0%, III = 3.2%.

**Complexation with Zinc(II).** Insertion of the zinc(II) ion into the "basket handle" porphyrin isomers I could not be accomplished. The free base porphyrin isomers II and III of the $n = 4$, 5, 6 "basket handle"

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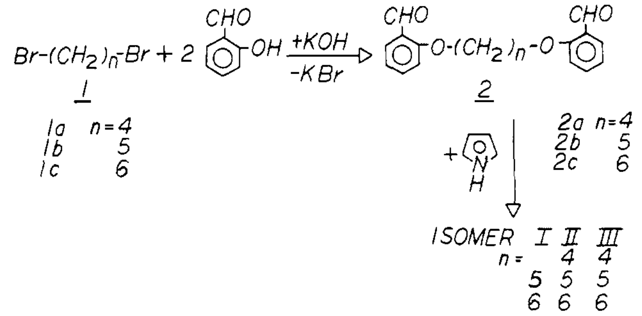
Scheme I



porphyrins (0.6 mmol) were each dissolved in a minimum amount of chloroform and heated to reflux. To each flask a solution of zinc(II) acetate dihydrate (1.8 mmol) in 20 mL of methanol was added dropwise and the reaction was allowed to reflux until no free base porphyrin was detectable (15 to 30 min depending on the isomer). The reaction mixture was cooled to room temperature and evaporated to dryness. The intensely red precipitate was thoroughly washed with hot water and then recrystallized in a mixture of toluene–ethyl acetate (1:1) to give red crystals of the zinc(II) "basket handle" porphyrin complexes.

**X-ray Structure Analysis.** The Zn(II) complex of isomer II ($n = 6$), hereafter referred to as Zn hexyl II, was prepared as described above and was obtained in crystalline form as the deuteriochloroform solvate by slow evaporation of a concentrated solution of the zinc complex in a NMR tube. After 3 weeks large red-purple crystals suitable for the X-ray diffraction study were deposited on the sides and the bottom of the sample tube. One of the crystals was mounted on a glass fiber and subjected to a detailed photographic examination followed by intensity data collection on an Enraf-Nonius CAD4 diffractometer. Details of the crystal data and intensity collection parameters at 296 K are given in Table V. Preliminary X-ray examination established a two-molecule monoclinic unit cell with systematic absences uniquely consistent with the space group $P2_1/n$. Least-squares refinement of the setting angles of 25 reflections led to the cell constants listed in Table V. Data reduction was performed as described previously.[18] The stability of the crystal was monitored during data collection by measurements of the intensities of three standard reflections after every hour of X-ray exposure. Over the course of data collection no significant change in intensity of any of these reflections was noted. No absorption correction was performed due to the small average value of $\mu t$.

The structure was solved with the direct methods program MULTAN78.[19] An $E$-map calculated from the largest 300 $E$ values gave the positions of the Zn atom, the 3 chlorine atoms of the $CDCl_3$ solvate molecule, all unique porphyrin core atoms, the 12 atoms of the phenyl rings, and most atoms in the alkoxy chain. The positions of the missing atoms were found in a subsequent difference Fourier synthesis. After several cycles of least-squares refinement, difference Fourier maps revealed the positions of all hydrogen atoms, except for the deuterium atom on the solvate molecule. These hydrogen atoms were included in subsequent least-squares refinement as fixed contributors (C–H = 0.96 Å). The isotropic thermal parameters of the hydrogen atoms were assumed to be 1.0 Å$^2$ larger than those of the carbon atoms to which they are attached ($B(\mathrm{H}) = B(\mathrm{C}) + 1.0$ Å$^2$).

Full-matrix least-squares refinement was then carried out to convergence for 331 variables which included anisotropic temperature factors for all heavy atoms. At convergence the final values for the discrepancy indices ($R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$) were $R_1 = 0.051$ and $R_2 = 0.068$. A difference Fourier map had its 6 highest peaks (0.6–1.0 e/Å$^3$) associated with the chloroform atoms; the map was judged to be otherwise featureless. The final fractional atomic coordinates are reported in Table VI. Bond length and angles involving the porphyrin core, the zinc atom, the phenyl groups and the alkoxy chain can be found in Table VIIa,b. Final anisotropic temperature factors are reported in Table VIIc (supplementary material). Tables of hydrogen atom positions and a listing of the final observed and calculated structure factor amplitudes are also available as supplementary material (Tables VIId and VIIe).

## Results

The synthesis of the parent hexyl-, pentyl-, and butyl-bridged so-called "basket handle" porphyrins based on a combination of Adler's,[14] Baldwin's,[15] and Momenteau's[13] synthetic route for sterically hindered porphyrins is outlined in Scheme I. Direct acid condensation of the dialdehydes **2a**, **2b**, and **2c** (synthesized from the potassium salt of salicylaldehyde and the commercially available dibromoalkyl derivatives **1a**, **1b**, and **1c**) with pyrrole in molar ratios of 1:2 led to the formation of the crude "basket handle" porphyrins, which were obtained as a mixture of different isomers. In order to minimize the formation of intermolecular polymerization products and to increase the yield of crude material very high dilution conditions (40 mL of acetic acid per 1 mmol of dialdehyde, twice as dilute as described by Momenteau[13]) were necessary. Bubbling oxygen through the reaction mixture prevented the formation of chlorins and, in the cases of the hexyl- and pentyl-bridged compounds, favored the formation of isomer I. Preparative thin-layer chromatography on silica gel plates showed no evidence for the formation of chlorins. If the reaction was carried out in the absence of oxygen the yield of all isomers was reduced about 10%. Furthermore, when no oxygen was present isomer I of the pentyl-bridged compund was not formed in any detectable yield.

TLC of the crude products showed that, except for the butyl-bridged "basket handle" porphyrins, three different isomers I, II, and III were formed as shown in Figure 1. For the $n = 4$ compound only isomers II and III could be obtained. The isomers were readily separated by column chromatography on silica gel with toluene or a mixture of toluene–hexane as eluent for the $n = 6$ compound, toluene or toluene–methylene chloride for the $n = 5$ compound, and methylene chloride and ethyl acetate for the $n = 4$ compound. The order of elution was I, II, and III. The first band which came down the column was the least polar isomer, I, as will be proven below.

Despite the strain apparent upon examination of space-filling molecular models, isomer I is formed in similar abundance for the $n = 6$ compound (I, 0.8%; II, 1.9%; III, 3.2%) as for the longer chain porphyrins synthesized by Momenteau and his co-workers.[13] However, for the $n = 5$ compound, both the overall yield and the amount of isomer I are significantly smaller (I, 0.2%; II, 2.9%; III, 1.6%) and the butyl-bridged isomer I was not formed in any detectable yield. Refluxing the reactants in acetic acid under nitrogen for 1 h followed by a second hour of reflux under an oxygen atmosphere also did not produce any detectable yield of butyl isomer I but changed the relative yields of the two other isomers (II 3.0% and III 3.2% compared to 1.8% and 4.4% obtained as described in the Experimental Section). This procedure should have allowed formation of the saturated ring precursor of the porphyrin, which would then have been oxidized to the porphyrin level upon refluxing in the presence of oxygen, if the butyl linkages could sustain the stretched conformation. Indeed, we were also not able to build a CPK model of isomer I for the butyl-bridged compound.

The structural assignment of the isomers (I, II, and III, Figure 1) was based on proton magnetic resonance and UV–vis spectroscopic data, their zinc(II) complex formation, as well as preliminary results of the X-ray crystal structure analysis of the hexyl-bridged isomer I[20] and the X-ray structure determination of the Zn(II) complex of isomer II of the hexyl-bridged compound described herein.

The electronic spectra of all new free base porphyrins and their zinc(II) complexes were routinely recorded and compared to those reported by Momenteau et al.[13] For the free base porphyrins the

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(19) Programs used in this study included local modification of Main et al.'s MULTAN78, Jacobson's ALLS, Busing and Levy's ORFFE and ORFLS, and Johnson's ORTEP2. Atomic factors were from Cromer and Mann (Cromer, D. T.; Mann, J. B. *Acta Crystallogr.* **1968**, *A24*, 321) with real and imaginary corrections for anomalous dispersion in the form factor of the zinc and chlorine atoms from the following: Cromer, D. T.; Liberman, D. J. *J. Chem. Phys.* **1970**, *53*, 1891. Scattering factors for hydrogen atoms were from the following: Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *Ibid.* **1965**, *42*, 3175.

(20) The free base porphyrin crystallizes in the monoclinic system, space group $P2_1/c$, with four molecules in the unit cell. At 296 K, the unit cell parameters are $a = 15.812$ (3) Å, $b = 21.532$ (5) Å, $c = 13.357$ (3) Å, and $\beta = 103.32$ (2)°. A detailed description of the structure has been hampered by significant side chain disorder. (Simonis, U.; Scheidt, W. R.; Walker, F. A., work in progress.)

**Table I.** Absorption Maxima (nm) of the Short Chain "Basket Handle" Porphyrins and Molar Absorption Coefficients (mol$^{-1}$ dm$^3$ cm$^{-1}$) in Parentheses[a]

| compound | Soret<br>B(0,0) | IV<br>$Q_y(1,0)$ | III<br>$Q_y(0,0)$ | II<br>$Q_x(1,0)$ | I<br>$Q_x(0,0)$ |
|---|---|---|---|---|---|
| hexyl I | 428 (228) | 526 (11.5) | 526 (5.1) | 602 (4.5) | 658 (1.7) |
| pentyl I | 438 (230) | 536 (11.0) | 576 (6.5) | 610 (4.8) | 668 (2.0) |
| butyl I | *b* | *b* | *b* | *b* | *b* |
| hexyl II | 420 (267) | 516 (16.8) | 548 (6.3) | 592 (5.6) | 646 (2.9) |
| pentyl II | 424 (271) | 518 (17.4) | 548 (7.5) | 596 (5.9) | 650 (2.9) |
| butyl II | 426 (252) | 520 (12.1) | 556 (4.5) | 604 (3.1) | 662 (3.3) |
| hexyl III | 422 (251) | 516 (13.7) | 550 (5.0) | 592 (4.3) | 646 (2.1) |
| pentyl III | 424 (255) | 520 (13.0) | 552 (5.1)[d] | 594 (4.5) | 648 (2.4)[c] |
| butyl III | 426 (253) | 520 (11.9) | 556 (4.2) | 604 (3.2) | 662 (2.6) |
| $(o\text{-}OCH_3)_4TPPH_2$[e] | 418 | 514 | 546 | 588 | 648 |
| $n = 10$[f] | | | | | |
| isomer I | 419 (390) | 513 (20.1) | 546 (6.2) | 591 (6.0) | 647 (2.8) |
| isomer II | 419 (398) | 513 (20.4) | 546 (6.4) | 591 (6.1) | 648 (2.9) |
| isomer III | 419 (366) | 513 (19) | 546 (6.8) | 592 (5.6) | 649 (3) |

[a] in dichloromethane solution. [b] This isomer was not obtained. [c] Ca. 3 nm broadening of this component. [d] Ca. 6 nm splitting of this component. [e] Mixture of atropisomers. [f] Values taken from ref 13.

**Table II.** Chemical Shifts of the Short Chain "Basket Handle" Porphyrins[a]

| compound | pyrrole-H | *o*-H | *p*-H | *m*-H | *m'*-H | *N*-H | $-OCH_2$ | β-$CH_2$ | γ-$CH_2$ |
|---|---|---|---|---|---|---|---|---|---|
| hexyl I | 8.75 | 8.85 | 7.58 | 7.58 | 6.91 | −0.84 | 2.49 | −1.13 | −2.07 |
| pentyl I | 8.80 | 8.88 | 7.58 | 7.52 | 6.87 | +0.18 | 0.88 | −1.09 | −2.44 |
| butyl I | *b* | *b* | *b* | *b* | *b* | *b* | *b* | *b* | *b* |
| hexyl II | 8.91, 8.69 | 8.20 | 7.73 | 7.42 | 7.31 | −2.58 | 3.73, 3.64 | 0.90, 0.18 | 0.18, 0.02 |
| pentyl II | 9.04, 8.66 | 8.36 | 7.72 | 7.43 | 7.15 | −2.55 | 3.90, 3.78 | 0.65, 0.55 | 0.96, 0.87 |
| butyl II | 9.24, 8.40 | 8.53 | 7.74 | 7.52 | 7.31 | −2.22 | 3.90 | 0.70, 0.25 | |
| hexyl III | 8.77, 8.68 | 8.13 | 7.72 | 7.38 | 7.32 | −2.54 | 3.81 | 1.20, 0.66 | 0.50, 0.45 |
| pentyl III | 8.69, 8.67 | 8.30 | 7.73 | 7.40 | 7.21 | −2.51 | 3.96, 3.86 | 0.86, 0.76 | 1.10, 1.06 |
| butyl III | 8.82, 8.38 | 8.47 | 7.74 | 7.48 | 7,30 | −2.09 | 3.97, 3.87 | 0.88, 0.60 | |
| $(o\text{-}CH_3)_4TPPH_2$[c] | 8.71 | 8.00 | 7.75 | 7.32 | 7,32 | −2.62 | 3.61, 3.57, 3.54 | | |

[a] In $CDCl_3$, chemical shifts in ppm from $Me_4Si$. Recorded at 21 °C. [b] This isomer was not obtained. [c] Mixture of atropisomers.

visible spectra taken in methylene chloride showed the satellite bands I–IV characteristic for porphyrins and the Soret band in the region of 420–430 nm.[21] The UV–vis spectra of the hexyl- and pentyl-bridged isomers II and III are comparable to those reported by Momenteau,[13] suggesting that the length of the alkoxy chain with five and six carbon atoms introduces essentially no distortion on the porphyrin ring in these isomers. That this is the case can also be seen from the results of the crystal structure analysis discussed below. In the electronic spectra of isomers II and III of the butyl-bridged compound significant change in the absorption maxima (red shift) was observed. This change was even more pronounced in isomer I of the $n = 5$ and 6 porphyrins, which implies significant distortion from planarity of the porphyrin ring, as will be discussed later. Table I lists the UV–vis spectral data; the electronic spectra of all free base porphyrin isomers are shown in Figure 2.

The proton magnetic resonance spectra proved especially informative about the structure of all compounds. It was possible to assign all proton signals. The phenyl ring proton resonances were assigned on the basis of selective homonuclear decoupling measurements while the N–H proton resonance was assigned by means of disappearance of the signal on $D_2O$ exchange. The large downfield shift of these N–H signals in some of the "basket handle" porphyrins suggests deformation of the porphyrin ring. The methylene bridge signals were particularly diagnostic and could be attributed to the corresponding methylene protons on the basis of selective homonuclear decoupling experiments and homonuclear shift correlated NMR spectroscopy (COSY). Figure 3 shows the NMR spectra of the hexyl- and butyl-bridged porphyrin isomers; the signal assignment for all protons is given in Table II.

To prepare a series of four-coordinate zinc(II) "basket handle" porphyrins the following strategy was employed: The isomers II and III of all free base porphyrins dissolved in chloroform were reacted with a methanolic solution of zinc(II) acetate dihydrate to give the desired zinc(II) porphyrin complexes. An excess of the metal(II) salt was used to complete the reaction until no free base was detected by either UV–vis spectroscopy or TLC. The reaction mixture was evaporated to dryness and washed repeatedly with water to remove the excess Zn(II) salt. Recrystallization in toluene or a mixture of toluene–ethyl acetate gave red-purple crystals of the zinc(II) complexes. Recrystallization in chloroform led to the decomposition of the metal complexes probably due to traces of hydrochloric acid in the solvent; starting material could be characterized.

**Table III.** Electronic Spectra Absorption Maxima (nm) of the Zinc(II) "Basket Handle" Porphyrins[a] and Molar Absorption Coefficients (mol$^{-1}$ dm$^3$ cm$^{-1}$) in Parentheses

| compound | Soret (nm)<br>B(0,0) | β-band (nm)<br>Q(1,0) | α-band (nm)<br>Q(0,0) |
|---|---|---|---|
| Zn hexyl II | 418 (5.9) | 550 (3.5) | 584 (0.8) |
| Zn hexyl III | 416 (5.8) | 550 (3.7) | 584 (0.7) |
| Zn pentyl II | 418 (6.5) | 550 (2.0) | 584 (0.5) |
| Zn pentyl III | 416 (5.9) | 550 (2.6) | 584 (0.7) |
| Zn butyl II | 426 (6.0) | 558 (2.3) | 600 (0.9) |
| Zn butyl III | 428 (5.9) | 558 (2.9) | 600 (0.8) |
| ZnTPP[b] | 419 (5.7) | 548 (4.3) | 589 (3.7) |

[a] The spectra were taken in dichloromethane. [b] The values are taken from ref 22 and 27.

We have been unable to metalate the free base porphyrin isomers I. Insertion of Zn(II) into these isomers could not be accomplished with use of the metal(II) acetate method or other common procedures such as the DMF method.[22] Steric hindrance may be responsible for preventing complex formation; the handles are obviously too short to allow the formation of the "sitting atop

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(21) Gouterman, M. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. III, pp 1–156.

(22) Buchler, J. W. In *Porphyrins and Metalloporphyrins*; Smith, K. M., Ed.; Elsevier Scientific Publishing Company: Amsterdam, 1975; pp 177–186.

**Table IV.** Chemical Shifts of the Zinc(II) Complexes of the "Basket Handle" Porphyrins[a]

| compound | pyrrole-H | *o*-H | *p*-H | *m*-H | *m'*-H | $-OCH_2$ | $\beta$-$CH_2$ | $\gamma$-$CH_2$ |
|---|---|---|---|---|---|---|---|---|
| Zn hexyl II | 8.96, 8.80 | 8.22 | 7.72 | 7.42 | 7.29 | 3.70, 3.60 | 0.86, 0.06 | 0.15 |
| Zn pentyl II | 9.14, 8.78 | 8.38 | 7.72 | 7.43 | 7.14 | 3.89, 3.75 | 0.51 | 0.99 |
| Zn butyl II | 9.28, 8.60 | 8.53 | 7.72 | 7.53 | 7.32 | 3.87 | 0.80, 0.28 | |
| Zn hexyl III | 8.90, 8.79 | 8.17 | 7.74 | 7.40 | 7.34 | 3.65 | 1.20 | 0.51 |
| Zn pentyl III | 8.85, 8.77 | 8.35 | 7.72 | 7.41 | 7.17 | 3.94, 3.71 | 0.86 | 1.16 |
| Zn butyl III | 8.93, 8.54 | 8.51 | 7.72 | 7.49 | 7.28 | 3.91, 3.86 | 0.89, 0.72 | |

[a] In $CDCl_3$ at 21 °C.

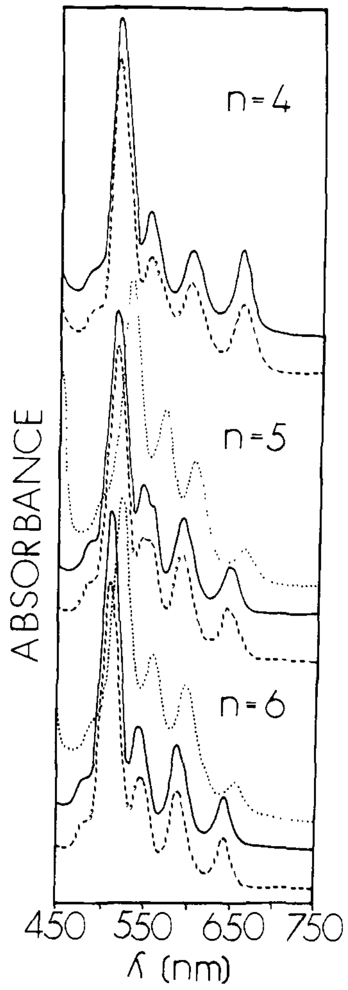

**Figure 2.** Electronic absorption spectra of all "basket handle" porphyrins showing red shift of isomer I and isomers II and III for $n = 4$: (···) isomer I; (—) isomer II; (---) isomer III.

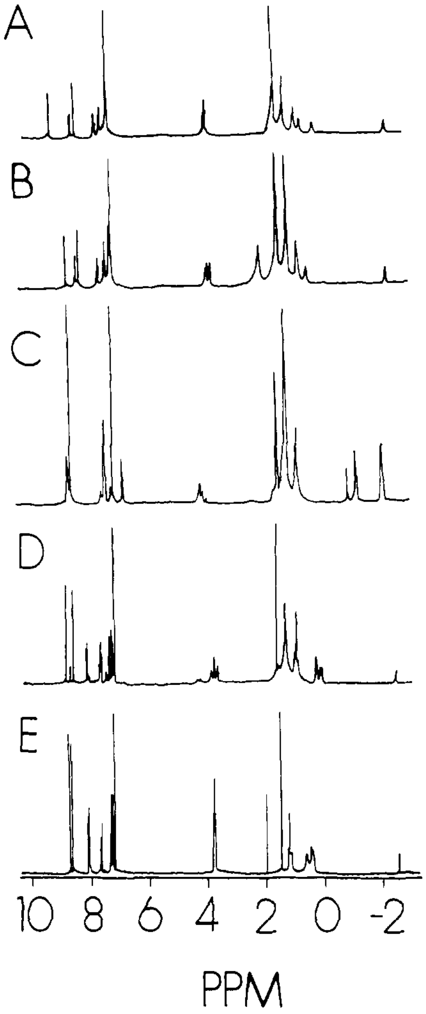

**Figure 3.** $^1H$ NMR spectra of the "basket handle" porphyrins: A = isomer II of $n = 4$; B = isomer III of $n = 4$; C = isomer I of $n = 6$; D = isomer II of $n = 6$; E = isomer III of $n = 6$.

complex" previously suggested to be an early step in metal insertion.[23] Attempted condensation of the dialdehydes and pyrrole in the presence of zinc(II) acetate dihydrate produced only metal-free porphyrins. Investigation is in progress to determine whether the Zn(II) isomer I complex can be obtained by starting from 5,10,15,20-tetrakis(2-hydroxyphenyl)-21*H*,23*H*-porphinezinc(II) followed by attachment of the bridge by reacting the Zn(II) porphyrin with the dibromoalkanes **1b** or **1c**.

The Zn(II) complexes of isomers II and III were characterized by UV-vis, $^1H$ NMR spectroscopy, and, in one case, X-ray crystallography. The electronic spectral data and the proton magnetic resonance spectroscopic data are listed in Tables III and IV, respectively. The crystallographic data of the Zn(II) complex of the hexyl-bridged isomer II are given in Tables V–VIIe (supplementary material). A projection of the molecular structure of the centrosymmetric Zn hexyl II molecule is given in figure 5 together with the labeling system for the crystallographically unique atoms of the coordination unit. The deviations from planarity of the porphyrin core atoms are presented in Figure 6, while selected bond distances and angles of the four-coordinate molecule are given in Table VIIa,b.

It is worth mentioning that only Zn(II) complexes of the hexyl isomers II and III could be obtained without difficulty in metal insertion. Diffraction studies of several single crystals confirmed the formation of only one isomer. Insertion of Co(II), Ni(II), and Fe(II) into either hexyl isomer II or III led to the formation of two structurally different complexes which could be characterized by $^1H$ NMR spectroscopy as a mixture of the metal complexes of isomers II and III. The chains of the hexyl-bridged porphyrin isomers II and III are thus apparently flexible enough to interconvert during the metalation process. Simply boiling the hexyl II isomer in toluene for 0.5 h led to the formation of both isomers II and III in equal amounts. None of these phenomena were observed for the pentyl or butyl derivatives. Time is a factor for the interconversion: Metalation with Zn(II) required only half the time necessary to insert Co(II), Ni(II), and Fe(II) into these porphyrins. This would require a concerted rotation of the phenyl

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[23] Hambright, P. In *Porphyrins and Metalloporphyrins*; Smith, K. M., Ed.; Elsevier Scientific Publishing Company: Amsterdam, 1975; pp 233–271.

**Table V.** Summary of Crystal Data and Intensity Collection Parameters for Zn Hexyl II

| | |
|---|---|
| chemical formula | $ZnCl_6O_4N_4C_{58}D_2H_{48}$ |
| formula weight (g mol$^{-1}$) | 1146.59 |
| crystal dimensions (mm) | 0.25 × 0.38 × 0.48 |
| color of the crystal | red-purple |
| temp (K) | 296 ± 2 |
| lattice parameters (Å, deg) | $a$ = 8.608 (2), $b$ = 22.212 (4), $c$ = 13.774 (2), $\beta$ = 91.90 (1) |
| unit cell vol (Å$^3$) | 2632.1 (14) |
| space group | $P2_1/n$ |
| $Z$ | 2 |
| density (obsd) (g cm$^{-3}$) | 1.443 |
| density (calcd) (g cm$^{-3}$) | 1.445 |
| radiation | Mo K$\alpha$ ($\lambda$ = 0.71073 Å) |
| monochromator | graphite crystal, incident beam |
| diffractometer | Enraf-Nonius CAD4 |
| scan technique | $\theta$–$2\theta$ |
| scan range in $2\theta$ (deg) | 0.8 + 0.35 tan ($\theta$) |
| scan rate (deg min$^{-1}$) | 2.0–4.0 |
| maximum $2\theta$ (deg) | 54.9 |
| criterion for observation | $F_o^2 > 3.0\sigma(F_o^2)$ |
| standard reflections | after every hour of X-ray exposure |
| unique obsd data | 3918 |
| final no. of variables | 331 |
| final no. of parameters | 673 |
| $\mu$(Mo K$\alpha$) (cm$^{-1}$) | 6.9 |
| $R_1$ | 0.051 |
| $R_2$ | 0.068 |

**Table VI.** Fractional Coordinates[a]

| atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Zn | 0.5000 | 0.5000 | 0.5000 |
| Cl(1) | −0.2917 (3) | 0.1603 (1) | 0.4375 (2) |
| Cl(2) | −0.2760 (2) | 0.0393 (1) | 0.5081 (1) |
| Cl(3) | −0.4955 (4) | 0.0738 (1) | 0.3578 (2) |
| O(1) | 0.9084 (3) | 0.3995 (2) | 0.2836 (2) |
| O(2) | 0.9131 (3) | 0.3492 (1) | 0.6647 (2) |
| N(1) | 0.4974 (3) | 0.5158 (1) | 0.3545 (2) |
| N(2) | 0.5852 (3) | 0.4162 (1) | 0.4778 (2) |
| C(a1) | 0.4438 (4) | 0.5669 (2) | 0.3075 (2) |
| C(a2) | 0.5402 (4) | 0.4764 (2) | 0.2831 (2) |
| C(a3) | 0.6156 (4) | 0.3905 (2) | 0.3892 (2) |
| C(a4) | 0.6173 (4) | 0.3733 (2) | 0.5465 (2) |
| C(b1) | 0.4532 (4) | 0.5586 (2) | 0.2042 (3) |
| C(b2) | 0.5119 (5) | 0.5037 (2) | 0.1896 (3) |
| C(b3) | 0.6660 (4) | 0.3292 (2) | 0.4045 (3) |
| C(b4) | 0.6653 (4) | 0.3185 (2) | 0.5006 (3) |
| C(m1) | 0.5993 (4) | 0.4184 (2) | 0.2991 (2) |
| C(m2) | 0.6073 (4) | 0.3811 (2) | 0.6473 (2) |
| C(1) | 0.6604 (4) | 0.3852 (2) | 0.2134 (2) |
| C(2) | 0.5636 (5) | 0.3623 (2) | 0.1397 (3) |
| C(3) | 0.6265 (6) | 0.3339 (2) | 0.0601 (3) |
| C(4) | 0.7861 (6) | 0.3273 (2) | 0.0552 (3) |
| C(5) | 0.8826 (5) | 0.3484 (2) | 0.1287 (3) |
| C(6) | 0.8201 (5) | 0.3776 (2) | 0.2073 (3) |
| C(7) | 0.6593 (4) | 0.3296 (2) | 0.7093 (3) |
| C(8) | 0.8170 (5) | 0.3134 (2) | 0.7145 (3) |
| C(9) | 0.8636 (5) | 0.2639 (2) | 0.7695 (3) |
| C(10) | 0.7577 (6) | 0.2314 (2) | 0.8196 (3) |
| C(11) | 0.6022 (6) | 0.2466 (2) | 0.8163 (3) |
| C(12) | 0.5538 (5) | 0.2958 (2) | 0.7615 (3) |
| C(13) | 1.0568 (5) | 0.4247 (2) | 0.2656 (3) |
| C(14) | 1.0971 (5) | 0.4678 (2) | 0.3477 (4) |
| C(15) | 1.1667 (5) | 0.4395 (2) | 0.4386 (3) |
| C(16) | 1.0639 (4) | 0.3964 (2) | 0.4946 (3) |
| C(17) | 1.1477 (5) | 0.3751 (2) | 0.5870 (3) |
| C(18) | 1.0640 (5) | 0.3270 (2) | 0.6420 (4) |
| C(19) | −0.333 (1) | 0.0867 (4) | 0.4141 (7) |

[a] The estimated standard deviations of the least significant digits are given in parentheses.

rings bearing the hexyl bridge toward each other in order to flip the bridge. Although this was an unexpected reaction the two isomers were clearly identifiable by TLC and NMR spectroscopy. Detailed studies of this interesting phenomenon are currently under way.

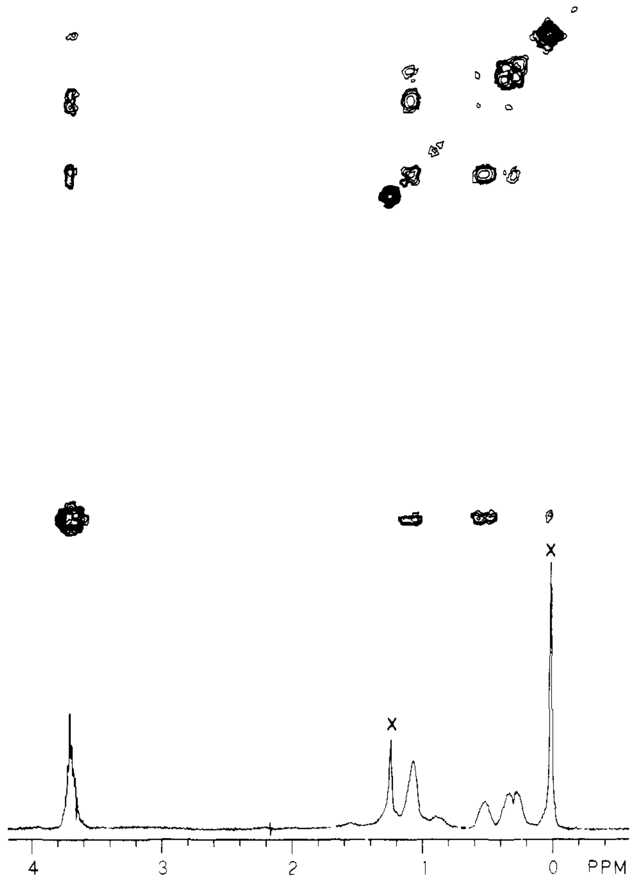

Figure 4. Expansion of the COSY spectrum of a sample of hexyl-bridged isomer III in $CS_2$, recorded without deuterium lock, showing the coupling pattern of the protons of the alkyl chains. The $\alpha$-$CH_2$ protons are coupled to each of the $\beta$-$CH_2$ protons, but only weak coupling is observed between the downfield $\beta$-CH proton and a $\gamma$-CH proton (the one further upfield). Two impurity peaks are marked X. The strong signal of the impurity at 0.05 ppm gives rise to an artifactual cross peak, as can be shown by examination of the unsymmetrical COSY data.

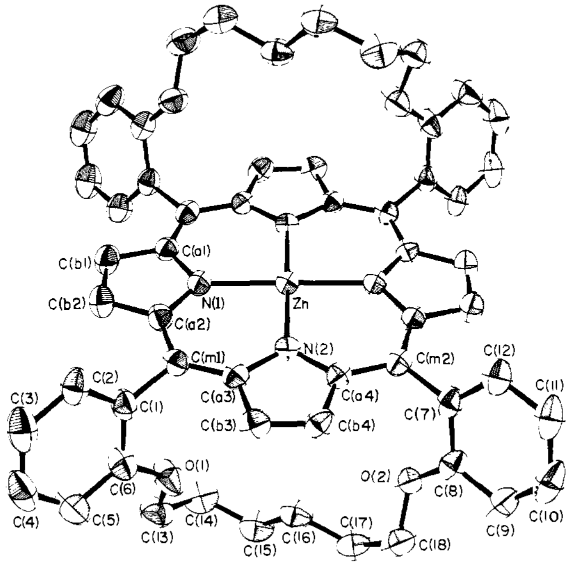

Figure 5. Computer-drawn model of Zn hexyl II. Atoms are presented by their vibrational ellipsoids contoured to enclose 50% of the electron density.

## Discussion

The properties of the short chain "basket handle" porphyrins of this study are significantly different from those reported for the longer handle analogues in terms of their spectroscopic and structural features.

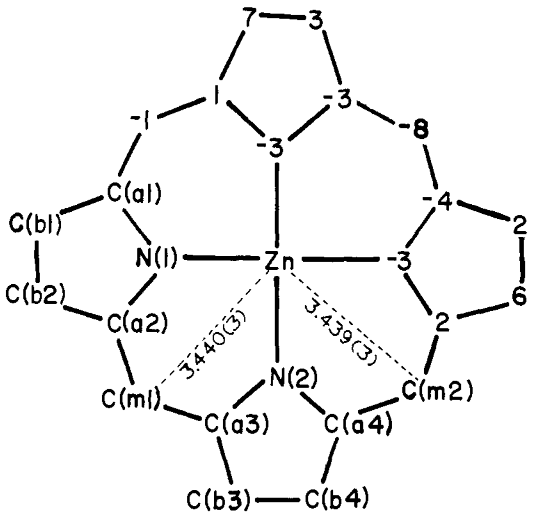

**Figure 6.** Formal diagram of the porphinato core of Zn hexyl II. Each atom has been replaced by the value of displacement of each atom, in units of 0.01 Å, from the 24-atom mean plane.

**UV–vis Spectroscopy.** As shown in Table I and Figure 2, the electronic spectral bands of isomer I for the $n = 6$ and 5 compounds are shifted 5 to 28 nm to the red of those of isomers II and III for the same compounds. The spectral bands of isomers II and III for the $n = 4$ free base porphyrin isomers are shifted 4–12 nm to the red of those of their respective longer chain analogues.[13] (The electronic spectra of the $n = 5$ and 6 isomers II and III differ only slightly as can be seen from Table I.) This suggests significant perturbations of the energies of the $A_{1u}(\pi)$, $A_{2u}(\pi)$, and $E_g(\pi^*)$ orbitals which are involved in these transitions.[21] Gouterman[21] has developed a molecular orbital theory which has been quite successful in explaining the occurrence and effects of substituents and metal coordination on the so-called Q and B bands of porphyrins and metalloporphyrins. In his terminology of the four-orbital model, the transitions that give rise to the characteristic porphyrin spectra bands are $A_{2u}(\pi) \rightarrow E_g(\pi^*)$ and $A_{1u}(\pi) \rightarrow E_g(\pi^*)$. The lowest energy exited singlet state Q(0,0) is split into $Q_x(0,0)$ and $Q_y(0,0)$ (bands I and III) by the $D_{2h}$ symmetry of the free base porphyrins. Each band has a vibronic overtone, $Q_x(1,0)$ and $Q_y(1,0)$ (bands II and IV, respectively).[24] The second excited singlet state B(0,0) gives rise to the B band (Soret band) which is not split due to the nodes that occur at the nitrogen atoms of the $A_{1u}(\pi)$ orbital.

By comparing the energies and intensities of Gouterman's Q and B bands and our porphyrin spectral bands of isomer I with those of isomers II and III, it appears that the porphyrin $\pi$ orbitals which are the most affected by the static distortion of isomer I are the $E_g(\pi^*)$ orbitals. This appears to be the case because all five major bands of isomers I are red shifted by a similar amount with the Soret band shifted only 2–6 nm less than bands I–IV (Table I). This is consistent with the symmetry of the $E_g(\pi^*)$ orbitals, which can be hybridized so as to place the nodes through opposite meso carbon positions for isomer I.[26] It is also apparent from examination of the data of Table I that for isomers II and III of the butyl-bridged compounds, the $Q_x$ transitions appear to be slightly more perturbed than the $Q_y$, as compared to the longer chain analogues. This suggests a greater splitting of the $E_g(\pi^*)$ orbitals in the butyl-bridged compounds, probably caused by static distortion of the porphyrin ring in these cases. Unfortunately, the low solubility of the butyl-bridged free bases and Zn(II) compounds has thus far prevented us from obtaining single crystals of sufficient size for X-ray diffraction studies. Efforts are continuing.

**Table VII.** Bond Distances[a] (Å) and Bond Angles[a] (deg) in the Coordination Group of the Porphinato Skeleton (A), in the Alkoxy Chain (B), and in the Phenyl Rings (C) of Zn hexyl II

(a) Bond Distances

| type | dist (Å) | type | dist (Å) |
|---|---|---|---|
| | A. Porphinato Skeleton | | |
| Zn–N(1) | 2.033 (3) | C(a3)–C(b3) | 1.443 (5) |
| Zn–N(2) | 2.028 (3) | C(a3)–C(m1) | 1.389 (5) |
| N(1)–C(a1) | 1.380 (4) | C(a4)–C(b4) | 1.439 (5) |
| N(1)–C(a2) | 1.375 (4) | C(a4)–C(m2) | 1.404 (5) |
| N(2)–C(a3) | 1.379 (4) | C(b1)–C(b2) | 1.339 (5) |
| N(2)–C(a4) | 1.364 (4) | C(b3)–C(b4) | 1.345 (5) |
| C(a1)–C(b1) | 1.439 (5) | C(m1)–C(1) | 1.502 (5) |
| C(a2)–C(b2) | 1.436 (5) | C(m2)–C(a1′) | 1.391 (5) |
| C(a2)–C(m1) | 1.402 (5) | C(m2)–C(7) | 1.488 (5) |
| | B. Alkoxy Chain | | |
| O(1)–C(6) | 1.365 (5) | C(14)–C(15) | 1.508 (6) |
| O(1)–C(13) | 1.424 (5) | C(15)–C(16) | 1.529 (6) |
| O(2)–C(8) | 1.353 (4) | C(16)–C(17) | 1.517 (6) |
| O(2)–C(18) | 1.434 (5) | C(17)–C(18) | 1.506 (6) |
| C(13)C(14) | 1.513 (6) | | |
| | C. Phenyl Rings | | |
| C(1)–C(2) | 1.387 (5) | C(7)–C(8) | 1.404 (5) |
| C(1)–C(6) | 1.390 (5) | C(7)–C(12) | 1.395 (5) |
| C(2)–C(3) | 1.391 (6) | C(8)–C(9) | 1.387 (5) |
| C(3)–C(4) | 1.386 (7) | C(9)–C(10) | 1.366 (6) |
| C(4)–C(5) | 1.370 (6) | C(10)–C(11) | 1.380 (6) |
| C(5)–C(6) | 1.388 (6) | C(11)–C(12) | 1.384 (6) |

(b) Bond Angles

| angle | value (deg) | angle | value (deg) |
|---|---|---|---|
| | A. Porphinato Skeleton | | |
| N(1)–Zn–N(2) | 180.0 (1) | N(2)–C(a4)–C(m2) | 125.6 (3) |
| N(1)–Zn–N(2′) | 90.1 (1) | N(2)–C(a4)–C(b4) | 109.9 (3) |
| N(1)–Zn–N(1′) | 89.9 (1) | C(m2)–C(a4)–C(b4) | 124.4 (3) |
| C(a1)–N(1)–C(a2) | 106.3 (3) | C(a1)–C(b1)–C(b2) | 107.3 (3) |
| C(a3)–N(2)–C(a4) | 106.6 (3) | C(a2)–C(b2)–C(b1) | 107.7 (3) |
| N(1)–C(a1)–C(m1) | 125.4 (3) | C(a3)–C(b3)–C(b4) | 107.5 (3) |
| N(1)–C(a1)–C(b1) | 109.3 (3) | C(a4)–C(b4)–C(b3) | 107.0 (3) |
| C(m2)–C(a1)–C(b1) | 125.3 (3) | C(a2)–C(m1)–C(a3) | 125.1 (3) |
| N(1)–C(a2)–C(m1) | 125.2 (3) | C(a3)–C(m1)–C(1) | 117.2 (3) |
| N(1)–C(a2)–C(b2) | 109.4 (3) | C(a2)–C(m1)–C(1) | 117.6 (3) |
| C(m1)–C(a2)–C(b2) | 125.3 (3) | C(a1′)–C(m2)–C(a4) | 125.1 (3) |
| N(2)–C(a3)–C(m1) | 126.2 (3) | C(a1′)–C(m2)–C(7) | 118.3 (3) |
| N(2)–C(a3)–C(b3) | 109.0 (3) | C(a4)–C(m2)–C(7) | 116.5 (3) |
| C(m1)–C(a3)–C(b3) | 124.8 (3) | | |
| | B. Alkoxy Chain | | |
| C(6)–O(1)–C(13) | 119.1 (3) | C(14)–C(15)–C(16) | 117.4 (3) |
| C(8)–O(2)–C(18) | 118.8 (3) | C(15)–C(16)–C(17) | 110.6 (3) |
| O(1)–C(13)–C(14) | 107.7 (3) | C(16)–C(17)–C(18) | 114.9 (4) |
| C(13)–C(14)–C(15) | 115.6 (4) | O(2)–C(18)–C(17) | 108.5 (3) |
| | C. Phenyl Rings | | |
| C(1)–C(2)–C(3) | 120.1 (4) | C(8)–C(7)–C(12) | 118.7 (3) |
| C(2)–C(1)–C(6) | 118.9 (3) | C(12)–C(7)–C(m2) | 121.4 (3) |
| C(2)–C(1)–C(m1) | 122.5 (3) | C(8)–C(7)–C(m2) | 119.9 (3) |
| C(6)–C(1)–C(m1) | 118.6 (3) | O(2)–C(8)–C(7) | 115.5 (3) |
| C(2)–C(3)–C(4) | 119.9 (4) | O(2)–C(8)–C(9) | 125.0 (4) |
| C(3)–C(4)–C(5) | 120.4 (4) | C(7)–C(8)–C(9) | 119.5 (4) |
| C(4)–C(5)–C(6) | 119.7 (4) | C(8)–C(9)–C(10) | 120.5 (4) |
| O(1)–C(6)–C(5) | 123.1 (4) | C(9)–C(10)–C(11) | 121.1 (4) |
| O(1)–C(6)–C(1) | 116.0 (3) | C(10)–C(11)–C(12) | 119.0 (4) |
| C(5)–C(6)–C(1) | 120.9 (4) | C(7)–C(12)–C(11) | 121.0 (4) |

[a] The numbers in parentheses are the estimated standard deviations.

Isomer I of the $n = 5$ compound is unique in the fact that it does not fluoresce as brightly as the other isomers under long-wave UV light. The weak fluorescence of this porphyrin could only be observed in the final step of silica gel purification. Any impurities present decreased the observed fluorescence.

The UV–vis spectra of the four-coordinate, square-planar zinc(II) porphyrin complexes are of the "normal type" and exhibit three bands as theoretically expected.[27] The most intense band

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(24) These absorption bands are mislabeled in an earlier publication.[25]

(25) Walker, F. A.; Balke, V. L.; McDermott, G. A. *Inorg. Chem.* **1982**, *32*, 2443.

(26) Walker, F. A. *J. Am. Chem. Soc.* **1980**, *102*, 3254.

in the UV region is denoted as the Soret band, and the other two less intense bands occurring in the region between 500 and 600 nm are denoted $\alpha$ and $\beta$. The wavelength of the $\alpha$ band, which is less intense than the $\beta$ band, appears to be correlated to bands I and III in the free base porphyrin spectra, while the $\beta$ band is correlated to bands II and IV.[27] According to Gouterman's four-orbital terminology[21] and transitions $A_{1u}(\pi)$, $A_{2u}(\pi) \rightarrow E_g(\pi^*)$ are largely responsible for the $\alpha$, $\beta$, and Soret bands. As can be seen from Table III, only the absorption bands of the Zn butyl II and Zn butyl III complexes are shifted by about 8–16 nm to the red compared to the longer chain analogues, with the $\alpha$ band being the most shifted. In comparison to the values reported for ZnTPP[22] these shifts are pronounced, while in comparison, the Zn pentyl and Zn hexyl porphyrin isomers II and III show only slight spectral shifts (maximum shift of 5 nm). Thus, as for the unmetalated porphyrins, only the Zn butyl-bridged complexes experience significant energy perturbations of the orbitals involved in the absorption processes.

**$^1$H NMR Spectroscopy.** The proton nuclear magnetic resonance spectra of all free base porphyrins and their zinc(II) analogues have proven essential in the identification of the three different "basket handle" porphyrin isomers. The $^1$H NMR spectra of isomers I of the hexyl- and pentyl-bridged porphyrins shown in Figure 3 are unique among tetraphenylporphyrins in that the *o*-phenyl protons occur downfield from the pyrrole protons at about 8.9 ppm, a downfield shift of 0.7 ppm from those of isomers II and III. This indicates significantly greater than normal deshielding of these *o*-phenyl protons and suggests that the phenyl rings are tipped in such a way as to place the *o*-phenyl protons more closely into the deshielding field of the porphyrin ring current. The N–H protons, which are assigned on the basis of $D_2O$ exchange, are also strongly perturbed in isomers I, in that they are less ring current shifted upfield than those of isomers II and III by ca. 1.7 ppm for the $n = 6$ and ca. 2.7 ppm for the $n = 5$ compound, whose N–H resonance signal occurs slightly downfield from $Me_4Si$ at +0,18 ppm. This indicates a large perturbation of the ring current at the central nitrogen atoms. Such a decrease in upfield ring current shift of the NH proton may suggest a contraction of the central hole size and/or shifting of considerable $\pi$-electron density to the peripheral portion of the aromatic macrocycle.

On the basis of symmetry, the eight pyrrolic protons in isomers I are expected to be equivalent; their signals therefore appear as a singlet at 8.75 ppm in the hexyl-bridged compound and at 8.80 ppm in the pentyl-bridged compound. Again, symmetry dictates that the resonances of the pyrrole protons of isomers II and III appear as two single peaks. On the basis of these symmetry considerations it is obvious that the alkoxy chains in isomers I span the porphyrin plane in a cross-linked arrangement, allowing for distinction of this isomer from the adjacent-cis-linked and the adjacent-trans-linked isomers. Interestingly the pyrrole proton signal of isomer I is not shifted significantly compared to the average proton chemical shift of isomers II and III, indicating that there is no major disruption of the peripheral ring current in isomer I. The minimum peak separation is 0.02 ppm in the pentyl-bridged isomer III, and the maximum is 0.84 ppm for the butyl II compound. The reason for the difference in separation of the two pyrrole proton peaks for isomers II and III for each different chain length is not clear. Small upfield shifts of all proton resonances are observed if $CS_2$ is used as solvent rather than $CDCl_3$. The largest shifts were observed for the pyrrole protons (0.15–0.18 ppm) and the N–H protons (0.16–0.25 ppm), but the separation between the pyrrole proton peaks for each isomer was independent of solvent.

The phenyl, pyrrole, and N–H resonance shifts for Momenteau's longer chain isomers I,[13] which exhibit no structural distortion of the porphyrin ring, are very similar to the values for the pentyl and hexyl isomers II and III reported in this paper. This suggests that the pentyl and hexyl isomers I described in the present study must be distorted from planarity, while the pentyl and hexyl isomers II and III exhibit no distortion. These conslusions are also supported by preliminary crystallographic results,[28] as well as the detailed structure determination described herein.

For isomers II and III of the $n = 4$ compound the *o*-phenyl proton signals appear between the two pyrrole peaks. This corresponds to a downfield shift of 0.17 ppm compared to the $n = 5$ isomers II and III and 0.34 ppm compared to the $n = 6$ compound. As in isomer I, this indicates greater deshielding interactions between the *o*-phenyl protons and the ring current. However, the N–H protons of these compounds do not exhibit the deshielding seen in isomer I. Therefore the distortion causing the *o*-phenyl protons to shift in isomers II and III cannot be the same as that experienced by isomer I.

The resonances of the chain protons in isomers I fell in the region of 2.49 to −2.44 ppm, a strong upfield shift relative to the corresponding methylene protons in the starting dialdehydes, indicating that these protons are more exposed to the diamagnetic anisotropy of the aromatic nucleus. The methylene protons of isomers II and III are not shifted upfield as much, which is also consistent with the structures proposed. These protons are assigned on the basis of selective homonuclear decoupling as well as COSY spectra of isomers II and III of the pentyl- and hexyl-bridged porphyrins. For hexyl-bridged isomers II and III, the $\beta$ protons appear at lower field than the $\gamma$ protons, while for the pentyl-bridged compounds the order is reversed. The methylene protons are all diastereotopic in isomers II and III, but in one case, that of isomer II of the butyl-bridged compound, the $-OCH_2-$ signal consists of one triplet due to all eight $\alpha$-$CH_2$ protons. In another case, that of hexyl III, the diasteriotopic $\alpha$-$CH_2$ signals are nearly superimposed. The individual $\alpha$-$CH_2$ resonances of the pentyl II and III compounds showed major coupling of the downfield proton to only one proton but coupling of the upfield $\alpha$-$CH_2$ proton to two protons. The hexyl II and butyl III compounds each showed slightly differently shaped multiplets for the two $\alpha$-$CH_2$ protons. All of these coupling patterns are indicative of specific Karplus relationships between the protons of adjacent methylene groups. The chemical shifts and coupling patterns for the methylene protons are also somewhat temperature dependent.

The COSY spectra of isomers II and III of the pentyl- and hexyl-bridged compounds were quite informative as to the coupling patterns involved in the alkyl chain. As shown in Figure 4, the downfield $\beta$-CH is coupled to the upfield $\gamma$-CH, while each $\beta$-CH of hexyl III is coupled to the $\alpha$-$CH_2$. Only a slight coupling is apparent between the $\beta$-CH and also $\gamma$-CH, probably due to an unfavorable Karplus relation. Cross peaks between the resonances of the $\gamma$ and $\beta$ CH protons are of low intensity, since the dihedral angle between these protons is close to 90°, as shown by molecular models and the structure of zinc hexyl II.

The perturbation of the ring current at the central nitrogen atoms is much larger for the distorted porphyrins of this study than that reported by Dolphin and co-workers[11] for their "pyrrole strapped" distorted porphyrins. From analysis of the NMR spectra it is quite clear that the N–H protons of isomers I, II, and III are not restricted to two of the four nitrogen atoms as in Dolphin's compounds,[11] in accord with symmetry predictions.

The proton nuclear magnetic resonance spectra of the diamagnetic zinc(II) complexes of isomers II and III provided additional support for the proposed structures. Coordination of the Zinc(II) ion to the four nitrogen atoms of the porphinato core resulted only in a downfield shift of the pyrrole signals of 0.1 to 0.2 ppm compared to the free base porphyrins due to the electron withdrawing effect of the metal. Downfield shifts of this order of magnitude upon complexation with the Zn(II) ion have been reported by several investigators.[4,29] The signals of the other

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[27] Buchler, J. W.; Kokisch, W.; Smith, P. D. *Struct. Bonding* **1978**, *34*, 80.

[28] Preliminary single-crystal X-ray structure results[20] for isomer I of the hexyl-bridged compound documents the deviation from planarity of the porphyrin ring in this isomer. In particular, the methine carbon atoms deviate up to 0.7 Å from planarity, alternating their displacements above and below the mean plane.

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**Table VIII.** Averaged Zn–N Bond Lengths in Structurally Characterized Four-, Five-, and Six-Coordinated Zinc(II) Porphyrin Complexes[a]

| zinc porphyrin complex | Zn–N distance (Å) | coordination no. | ref |
|---|---|---|---|
| Zn hexyl II | 2.031 (3) | 4 | this work |
| $ZnTPP{\cdot}2C_6H_5CH_3$ | 2.036 (6) | 4 | 31 |
| ZnTPP | 2.037 (2) | 4 | 32 |
| Zn($\alpha$-$NO_2$-OEP) | 2.039 | 4 | 33 |
| $ZnTPP(THF)_2$ | 2.057 (1) | 6 | 34 |
| ZnOEP(Py) | 2.067 (6) | 5 | 35 |
| $ZnTPP(OClO_3)$ | 2.076 (9) | 5 | 36 |
| $ZnTPP(H_2O)$ | 2.05 (1) | 5 | 37 |
| $ZnTPP(NHCOCH_2CH_2Py)$ | 2.063 (11) | 5 | 38 |
| ZnTPyP(Py) | 2.073 (6) | 5 | 30a |
| ZnTPC(Py) | 2.065 (6)[b] | 5 | 39 |
| ZnTPiBC(Py) | 2.070 (13)[b] | 5 | 40 |

[a] Root-mean-square standard deviations are given in parentheses for the least significant digit. [b] Average of the porphyrinic Zn–N bonds.

protons in the Zn(II) complexes are not influenced by the insertion of the zinc atom and appear at almost identical chemical shifts to those of the free base analogues, as can be seen by comparing the values in Table II and Table IV.

It was not possible to unambiguously assign structures of the isomers labeled II and III to the adjacent-cis-linked and -trans-linked structures based on the NMR results alone. Therefore we investigated the crystal structure of the zinc complex of isomer II of the hexyl-bridged "basket handle" porphyrin.

**X-ray Structure Analysis.** The X-ray structure of the Zn hexyl II complex confirmed the results obtained from the spectroscopic investigations. On the basis of these results it can be clearly shown that (a) the handles are above and below the porphinato plane, (b) the interconversion of the handles is not observed in this isomer, and (c) the porphinato ring is quite planar.

The molecular structure of the coordination unit for the zinc hexyl II complex is illustrated in Figure 5, together with the labeling system for the crystallographically unique atoms. As can be seen from the thermal ellipsoid plot, the zinc atom is bound to the four nitrogen atoms of the macrocycle in a square-planar arrangement. The central atom occupies a special position of the space group, the inversion center, and is therefore precisely centered in the hole of the porphinato core. Although it has previously been thought, as a result of spectroscopic and binding constants studies,[30] that the relatively large size of the Zn(II) ion precludes its being positioned in the mean porphyrin plane, this structure is another example demonstrating the capability of the Zn atom to occupy such a position. The Zn atom can be "squeezed" into the porphinato hole, as has also been shown[31] for the toluene solvate of ($\alpha,\beta,\gamma,\delta$-tetraphenylporphinato)zinc(II).

With the two unique Zn–N distances of 2.028 (3) and 2.033 (3) Å (average value of 2.031 (3) Å), the complex exhibits a somewhat compressed metal–nitrogen bond length. The average Zn–N distance is the shortest reported for structurally characterized four-coordinate zinc porphyrin complexes (Table VIII). However, it is not significantly shorter than those reported for solvated and unsolvated ZnTPP.[31,32] (A detailed discussion of Zn–N distances is given by Scheidt and co-workers.[31]) Nevertheless the short Zn–N distance may be a sign of the reduction of the porphyrin core size. As also concluded by Scheidt et al.,[32] the 2.03–2.04 Å average distance represents the best value for the unconstrained molecule.

**Table IX.** Comparative Structural Analyses of Distances (Å) and Angles (deg) in Zinc Porphyrin Complexes

| parameters | ZnTPP[a] | $ZnTPP{\cdot}2C_6H_5CH_3$[b] | Zn hexyl II |
|---|---|---|---|
| Zn–N(av) | 2.037 | 2.036 | 2.031 |
| N–C(a) | 1.375 | 1.376 | 1.375 |
| C(a)–C(b) | 1.443 | 1.438 | 1.439 |
| C(b)–C(b) | 1.351 | 1.351 | 1.342 |
| C(a)–C(m) | 1.399 | 1.408 | 1.397 |
| C(a)–N–C(a) | 106.5 | 106.4 | 106.5 |
| N–C(a)–C(b) | 109.6 | 109.6 | 109.6 |
| C(a)–C(b)–C(b) | 107.2 | 107.3 | 107.4 |
| N–C(a)–C(m) | 125.7 | 125.7 | 125.9 |
| C(a)–C(m)–C(a) | 125.0 | 124.8 | 125.1 |
| C(m)–C(a)–C(b) | 124.7 | 124.5 | 124.6 |

[a] Data taken from ref 32. [b] Data taken from ref 31.

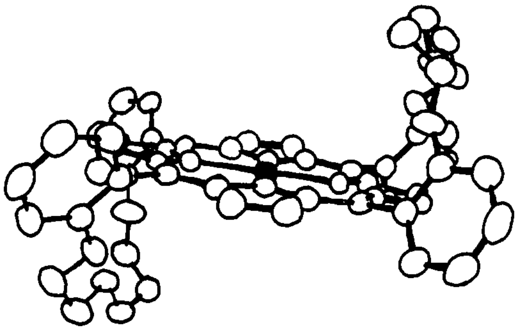

**Figure 7.** Illustration showing the position of the alkoxy chains of Zn hexyl II. From this view it is clear that the alkoxy chains should not interfere significantly with axial ligand binding, but may interfere with rotation of planar axial ligands of sufficient size.

All C–C and C–N distances of the porphyrin ligand are similar to values reported for solvated and unsolvated ZnTPP.[31,32] With use of C(a) and C(b) to denote the $\alpha$ and $\beta$ carbon atoms of the pyrrole heterocycles and C(m) for the methine carbon atoms, averaged bond distances and angles for the Zn hexyl II and the ZnTPP complexes are given in Table IX. The numbers in parentheses for each averaged value are the estimated standard deviations.

As concluded from the UV–vis and $^1H$ NMR spectroscopic studies discussed above, the macrocycle itself is essentially planar, as depicted in Figure 6, with the largest displacement from the mean porphyrin plane at C(m1) and C(b1) of 0.08 and 0.06 Å. The dihedral angle between the planes of the two adjacent pyrrole rings is 5.1°. The five-membered chelate ring formed by the Zn atom and each two of the four nitrogen atoms of the macrocycle is also quite planar. Overall the deviations from planarity are small and consistent with values reported for ZnTPP.[31] Thus, a chain length of six carbon atoms introduces no strain onto the porphyrin ring, if the alkoxy chains are bridging two adjacent phenyl rings through their ortho positions.

The phenyl rings connected by the alkoxy bridges are tipped toward each other, with average dihedral angles to the mean porphyrin plane of 81°. The shortest distances are C(2)–C(9) = 3.771 (6) Å and C(5)–C(12) = 3.949 (7) Å.

As illustrated in Figure 5 and more clearly in Figure 7, the alkoxy chains bridge two adjacent phenyl rings above and below the mean porphyrin plane and introduce no distortion in the porphyrin ring. The methylene groups extend far above and below the porphyrin plane. The shortest contact between a chain atom

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and the macrocycle is C(16)$\cdots$C(b4) = 3.846 (5) Å; all other distances are larger. Thus the bridging alkyl chains of isomers II and III are not expected to interfere significantly with the binding of axial ligands, although they may interfere with free rotation of bound axial ligands about the M–L bond. Preliminary NMR investigations of low-spin Fe(III) complexes of hexyl II and III with N-MeIm suggest that this is the case, as will be discussed fully in a later publication,

**Acknowledgments.** The financial support of the National Institutes of Health [Grants AM 31038 (F.A.W.) and HL 15627 (W.R.S.)] is gratefully acknowledged. This work has also been supported by a NATO grant for scientific investigation, administered by the DAAD, West Germany (U.S.), and by a NATO grant for scientific investigation, administered by GNAM-OTAN, France (B.J.H.). B.J.H. also acknowledges receipt of a research leave from the University of Dijon. The Department of Chemistry, San Francisco State University, also acknowledges grants from the National Institutes of Health (RR 02684) and the National Science Foundation (DMB-8516065) for purchase of the NMR spectrometers. Some NMR spectra were recorded on the Nicolet NT-360 at the University of California, Davis, NMR facility, and on the Bruker WM-500 at the University of California, Berkeley. X-ray crystal structure analyses were performed at the University of Notre Dame. The authors also thank Dr. Charles W. Eigenbrot for collecting the data set for Zn hexyl II.

**Supplementary Material Available:** Tables of anisotropic thermal parameters, fractional coordinates, and isotropic thermal parameters (2 pages); listing of observed and calculated structure factors (13 pages). Ordering Information is given on any current masthead page.

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# Dioxygen–Copper Reactivity. Reversible Binding of $O_2$ and CO to a Phenoxo-Bridged Dicopper(I) Complex

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**Abstract:** A chemical system possessing features that mimic certain structural properties and the $O_2$ binding behavior of the active site of the copper-containing dioxygen carrier hemocyanin (Hc) is presented. A phenolic dinucleating ligand possessing two tridentate py2 units (py2 = bis(2-(2-pyridyl)ethyl)amine) (XYL-OH) forms a phenoxo-bridged dicopper(I) complex, $[Cu_2(XYL\text{-}O\text{-})]PF_6$ (**1**). At −80 °C in dichloromethane solution, **1** reacts with $O_2$ (Cu:$O_2$ = 2:1) to give an intensely purple-colored dioxygen adduct, $[Cu_2(XYL\text{-}O\text{-})(O_2)]PF_6$ (**2**), having charge-transfer absorptions in the visible region at 505 ($\epsilon$ 6000) and 610 (sh) nm ($\epsilon$ 2100 $(M{\cdot}cm)^{-1}$) with additional features at 385 ($\epsilon$ 2900), 790 ($\epsilon$ 700), and 925 nm ($\epsilon$ 600 $(M{\cdot}cm)^{-1}$). The binding of $O_2$ to **1** is reversible, and the $O_2$ ligand can be removed in vacuo to regenerate **1**. This *vacuum cycling* can be followed spectrophotometrically over several cycles. Carbon monoxide and triphenylphosphine react with **1** to form the bis adducts **3**, $[Cu_2(XYL\text{-}O\text{-})(CO)_2]PF_6$ (**3a**) and $[Cu_2(XYL\text{-}O\text{-})(PPh_3)_2]PF_6$ (**3b**), respectively; the reaction with carbon monoxide is also reversible. The dioxygen adduct **2** reacts with CO and/or $PPh_3$, displacing the bound $O_2$ ligand and producing the adducts **3**; this behavior further substantiates that the reaction of **1** with $O_2$ is an equilibrium process. *Carbonyl cycling*, where **1** reacts with $O_2$ to produce **2**, $O_2$ is displaced by CO to produce **3a**, and **3a** is decarbonylated to regenerate **1**, can also be followed spectrophotometrically over several cycles. In both cycling procedures, a decomposition product is observed and identified as the phenoxo and hydroxo doubly bridged dicopper(II) complex $[Cu_2(XYL\text{-}O)(OH)]^{2+}$. Crystallographic studies have been completed for both **1** and **3b**. **1** crystallizes in the monoclinic space group $P2_1/n$ with $Z = 8$ (2 per asymmetric unit) and $a = 13.861$ (4) Å, $b = 13.482$ (8) Å, $c = 16.956$ (5) Å, and $\beta = 98.20$ (2)°. Complex **3b** crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$ and $a = 13.410$ (3) Å, $b = 14.867$ (3) Å, $c = 18.990$ (4) Å, $\alpha = 102.35$ (2)°, $\beta = 91.71$ (2)°, and $\gamma = 98.68$ (2)°. While **1** contains two phenoxo-bridged tetracoordinate Cu(I) ions (Cu$\cdots$Cu = 3.62–3.72 Å) where each copper atom is also coordinated to the py2 tridentate group, in **3b** one pyridine donor from each py2 unit remains uncoordinated such that each Cu(I) atom is bound by two nitrogen donors, the P atom from a $PPh_3$ ligand, and the bridging phenoxo oxygen atom (Cu$\cdots$Cu = 3.992 Å).

The interest in understanding the binding, interaction, and subsequent reactivity of dioxygen ($O_2$) at copper ion centers stems in part from the occurrence of copper-containing enzymes such as hemocyanin (Hc),[1-5] which transports $O_2$, and the monooxygenases tyrosinase[1,2b,4-6] and dopamine $\beta$-hydroxylase,[1,2b,4-7] which incorporate oxygen (from $O_2$) into organic substrates. Studies of biomimetic chemical models can be useful in determining the relevant and/or possible coordination chemistry in the proteins and thus help to elucidate structural and spectroscopic properties of the enzyme active sites.[4,5,8] Concepts derived from such studies may also be expected to contribute to the development of practical synthetic systems for the reversible binding of $O_2$

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