Synthesis, Crystal Structures, and Redox Potentials of 2,3,12,13-Tetrasubstituted 5,10,15,20-Tetraphenylporphyrin Zinc(II) Complexes

Yuichi Terazono, Brian O. Patrick, and David H. Dolphin*

Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, BC, Canada

Received May 13, 2002

Metalloporphyrins in Catalytic Oxidations

Zinc(II) complexes of antipodal β-tetrasubstituted meso-tetraphenylporphyrin with trifluoromethyl (Zn(TPP(CF3)4) (1a)), bromine (Zn(TPPBr4) (2a)), and methyl groups (Zn(TPP(CH3)4) (3a)) were synthesized in order to examine the steric and the electronic effects of trifluoromethyl groups on the macrocycle. The analysis of X-ray crystal structures of the five-coordinate complexes Zn(TPP(CF3)4)(EtOH)3 (1b), Zn(TPPBr4)(MeOH)(DMF) (2b), and Zn(TPP(CH3)4)(THF)1,5(CHCl3)0.4 (3b) revealed distorted macrocyclic cores where significant differences in the Zn–N distance between the β-substituted and the non-β-substituted side were observed. The difference was significant in 1b due to the strong steric interactions among the peripheral substituents and the electronic effects of trifluoromethyl groups. The macrocycles of 1b–3b are saddle-distorted and slightly ruffled due to the five-coordination of zinc(II) and the peripheral substitution. Distortion of the macrocycles of 2b and 3b were modest. On the other hand, distortion in 1b was severe due to the peripheral strain. Cyclic voltammetric measurements of the four-coordinate complexes Zn(TPP) and 1a–3a were performed and their redox potentials were analyzed together with previously reported potentials of Zn(TPP(CN)4). The oxidation potential of 1a did not gain as much as expected from the electron-withdrawing effect of the four trifluoromethyl groups. The magnitude of this gap is very similar to that of Zn(TPP(CN)4). Compound 2a also exhibited a modest gap contraction. Compound 3a was easier to oxidize and harder to reduce than Zn(TPP), even though the HOMO–LUMO gap of 3a was similar to that of Zn(TPP).

Introduction

Synthetic porphyrins used in model studies of hemoproteins have been prepared using design strategies involving both structural and electronic modifications. For example, model studies of hemoglobins and myoglobins were driven by sterically hindered synthetic porphyrins into a successful globin-like control of axial ligand coordination.1–3 Recent examples of structurally modified porphyrins have been involved in studies concerning nonplanarity of the porphyrin macrocycle whose link to the functions of hemoproteins has been suggested.4–7 Meanwhile, electronically and sterically modified porphyrins, especially incorporating strongly electron-withdrawing substituents, have focused on catalytic oxidations in order to mimic and improve their cytochrome P-450-like activity.8–10 So far various porphyrins bearing electron-withdrawing substituents such as pentachlorophenyl, pentafluorophenyl, perfluoroalkylphenyl, fluoro, chloro, bromo, cyano, nitro, or perfluoroalkyl groups on meso and/or pyrrolic β-positions of the porphyrin macrocycle have been syn-

References:

Electron-withdrawing and bulky trifluoromethyl groups in $\beta$-trifluoromethyl-meso-tetraphenylporphyrins dramatically alter the properties of the macrocycle and provide stable porphyrin ligands. In addition, perfluoroalkyl porphyrins are soluble in a wide range of solvents and may be useful as catalysts in special media.

### Experimental Section

**Materials.** All chemicals were purchased from Sigma-Aldrich fine chemicals, Across Chemicals, or Fisher Scientific. Deuterated solvents for NMR measurements were purchased from Cambridge Isotope Laboratories. Chlorinated solvents were filtered using neutral alumina (Fisher, activity I) to remove trace acid. Methylene chloride for cyclic voltammetric measurements was distilled from anhydrous neutral alumina (Fisher, activity I) to remove trace acid. Methylene chloride was distilled from sodium under argon atmosphere. All chemicals were purchased from Sigma-Aldrich.

**Instrumentation.** UV–vis spectra were recorded on a Varian Cary 50 scan UV–visible spectrophotometer. NMR spectra were recorded on Bruker AC-200 or Avance 300. Cyclic voltammetric measurements were performed with a single-compartment electrochemical cell, a Pine Instrument Co. bipotentiostat model AFCBP1, and a Pine Chem sweep voltammetry software for Windows ver. 2.00.

**Preparation of Zn(II) Complexes.** In most cases, Zn(II) complexes were prepared as described previously. For the synthesis of metalloporphyrins, LR-MS (EI, 300 °C): $M^{+}$ (m/z) = 993; for $\text{C}_{40}\text{H}_{22}\text{Br}_{4}\text{N}_{4}\text{Zn}$: $\lambda_{\text{max}}$ (nm) 430, 560, 598. $^1\text{H}$ NMR (DMSO-$d_6$): 6.43 (s, 8H, pyrrole-CH$_3$). $^1\text{H}$ NMR (CDCl$_3$): 6.37 (m, 16H, phenyl-$o$- and -m), 8.05 (m, 8H, phenyl-$p$-H), 8.03 (s, 4H, pyrrole-$\beta$-H). $^1\text{H}$ NMR (CDCl$_3$): 7.09 (m, 16H, phenyl-$o$- and -m), 7.98 (s, 8H, pyrrole-$p$-H). CHN anal. (%), calcd for $\text{C}_{40}\text{H}_{22}\text{Br}_{4}\text{N}_{4}\text{Zn}$: C, 53.25; H, 2.54; N, 5.42. Found: C, 53.25; H, 2.54; N, 5.49.

**Examples.**

- **Example 1:**

  $\text{Zn(II)}$ was inserted into $\text{H}_2\text{TPP}$ by a standard procedure.

- **Example 2:**

  UV–vis (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ (nm) 419, 548, 582. $^1\text{H}$ NMR (CDCl$_3$): 6.37 (m, 16H, phenyl-$p$, -$p$, and -m), 7.98 (s, 8H, pyrrole-$\beta$, -$\beta$-H).

- **Example 3:**

  UV–vis (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ (nm) 420, 534, 573. $^1\text{H}$ NMR (DMSO-$d_6$): 6.31 (s, 4H, pyrrole-$H$), 7.98 (m, 16H, phenyl-$o$- and -m), 7.95 (s, 8H, pyrrole-$p$-H). CHN anal. (%), calcd for $\text{C}_{40}\text{H}_{22}\text{Br}_{4}\text{N}_{4}\text{Zn}$: C, 53.18; H, 2.43; N, 5.64. Found: C, 53.25; H, 2.54; N, 5.42.

- **Example 4:**

  UV–vis (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ (nm) 420, 534, 573. $^1\text{H}$ NMR (DMSO-$d_6$): 6.31 (s, 4H, pyrrole-$H$), 7.98 (m, 16H, phenyl-$o$- and -m), 7.95 (s, 8H, pyrrole-$p$-H). CHN anal. (%), calcd for $\text{C}_{40}\text{H}_{22}\text{Br}_{4}\text{N}_{4}\text{Zn}$: C, 53.18; H, 2.43; N, 5.64. Found: C, 53.25; H, 2.54; N, 5.42.

- **Example 5:**

  UV–vis (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ (nm) 420, 534, 573. $^1\text{H}$ NMR (DMSO-$d_6$): 6.31 (s, 4H, pyrrole-$H$), 7.98 (m, 16H, phenyl-$o$- and -m), 7.95 (s, 8H, pyrrole-$p$-H). CHN anal. (%), calcd for $\text{C}_{40}\text{H}_{22}\text{Br}_{4}\text{N}_{4}\text{Zn}$: C, 53.18; H, 2.43; N, 5.64. Found: C, 53.25; H, 2.54; N, 5.42.
Table 1. Crystallographic Data for 1b–3b

<table>
<thead>
<tr>
<th></th>
<th>1b</th>
<th>2b</th>
<th>3b</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>C48H35Br4N5</td>
<td>C48H35Br4N5</td>
<td>C54H48O26N6Cl20</td>
</tr>
<tr>
<td>O</td>
<td>ZnO</td>
<td>ZnO</td>
<td>ZnO</td>
</tr>
<tr>
<td>fw</td>
<td>1088.31</td>
<td>1098.83</td>
<td>897.34</td>
</tr>
<tr>
<td>space group</td>
<td>P1 (No. 2)</td>
<td>P1 (No. 2)</td>
<td>P221/n (No. 14)</td>
</tr>
<tr>
<td>a (Å)</td>
<td>12.0428(11)</td>
<td>12.257(2)</td>
<td>13.585(1)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>13.275(2)</td>
<td>13.4377(8)</td>
<td>18.182(1)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>16.9099(2)</td>
<td>13.487(1)</td>
<td>18.065(2)</td>
</tr>
<tr>
<td>α (deg)</td>
<td>96.9515(5)</td>
<td>83.819(2)</td>
<td></td>
</tr>
<tr>
<td>β (deg)</td>
<td>108.124(2)</td>
<td>71.227(2)</td>
<td>93.274(3)</td>
</tr>
<tr>
<td>γ (deg)</td>
<td>107.354(2)</td>
<td>73.575(3)</td>
<td></td>
</tr>
<tr>
<td>V (Å³)</td>
<td>2383.2(5)</td>
<td>2151.75(3)</td>
<td>4454.9(6)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Dcalc (g/cm³)</td>
<td>1.52</td>
<td>1.70</td>
<td>1.34</td>
</tr>
<tr>
<td>μ(Mo Kα) (em⁻¹)</td>
<td>6.13</td>
<td>43.42</td>
<td>67.00</td>
</tr>
<tr>
<td>T(℃)</td>
<td>80.0</td>
<td>-93.1 ± 1</td>
<td>-100 ± 1</td>
</tr>
<tr>
<td>no. of indep reflns</td>
<td>10728</td>
<td>8177</td>
<td>7452</td>
</tr>
<tr>
<td>I &gt; 3o(I)</td>
<td>5823</td>
<td>6086</td>
<td>2621</td>
</tr>
<tr>
<td>no. of obsd reflns</td>
<td>5823</td>
<td>6086</td>
<td>2621</td>
</tr>
<tr>
<td>R₁</td>
<td>0.053</td>
<td>0.033</td>
<td>0.051</td>
</tr>
<tr>
<td>Rw</td>
<td>0.091</td>
<td>0.089</td>
<td>0.155</td>
</tr>
</tbody>
</table>

551, 587sh. 1H NMR (CDCl₃): δ 0.34 (s, 12H, –CH₃), 7.75 (m, 12H, phenyl-m- and -pH), 8.06 (m, 8H, phenyl-o-H), 8.65 (s, 4H, pyrR-β-H).

Zn(TPP(CF₃)₄)(CH₃OH)(1b). Zn(TPP(CF₃)₄)(1a) was dissolved in a 50:50 chloroform:ethanol solution, and crystallization of 1b was induced by slow evaporation at room temperature. After a period of 2 weeks, purple crystals were obtained. 1H NMR (CDCl₃): δ 0.34 (t, 3H, EtOH (–OH)), 0.73 (t, 3H, EtOH (–CH₂–)), 2.94 (m, 6H, EtOH (–CH₂–)), 1.70 (m, 12H, phenyl-m- and -pH), 1.08 (m, 8H, phenyl-o-H), 1.37 (s, 4H, pyrR-β-H). 13C NMR (CDCl₃): δ (vs CFCl₃): 44.36. UV–vis (CHCl₃) (log e): 444 (5.42), 583h (5.58), 664 (4.34). CHN anal. (%), calcd for C₅₉H₉₉Br₂N₆O₁₂ZnO₁₂: C, 52.60; H, 3.64; N, 5.02. Found: C, 60.00; H, 3.64; N, 5.02.

X-ray Crystallography. All measurements were made on a Rigaku/ADSC CCD area detector with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). Crystal data and details of the diffraction data collections are given in Table 1. The data were collected at –93 ± 1, –100 ± 1, and –100 ± 1 ºC to a maximum 2θ value of 60.2°, 55.7°, and 50.1° at 0.50º oscillations with 80.0, 12.0, and 58.0 s exposures for 1b–3b, respectively. A sweep of data was performed using φ oscillations from 0.0° to 190.0° at χ = –90.0°, –90.0°, and 0.0°, and a second sweep was performed using ω oscillations between –23.0° and 18.0°, –19.0° and 23.0°, and –19.0° and 23° at χ = –90.0° for 1b–3b, respectively. The structures were solved by heavy-atom Patterson methods for 1b and by direct methods for 2b and 3b and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The OH hydrogen atom of the coordinated ethanol was refined isotropically. In 3b, one disordered molecule of THF coordinated to Zn(II); in addition, two different solvents, THF and CHCl₃, partially occupy the same volume in the asymmetric unit. In 3b, all the disordered solvent molecules were refined isotropically, while all other atoms were refined anisotropically. All calculations were performed using the teXsan crystallographic software package.37

Results and Discussion

X-ray Crystal Structures. ORTEP views of the crystal structures for Zn(TPP(CF₃)₄)(EtOH) (1b), Zn(TPPBr₄)(MeOH)(DMF) (2b), and Zn(TPP(CH₃)₄)(CHCl₃)(THF) (3b) are shown in Figure 1. Selected bond lengths and bond angles for the three molecules together with previously reported data for pentacoordinated Zn(TPP)(H₂O) are summarized in Table 2.

Coordination around Zn(II) in 1b–3b is pentacoordinate square pyramidal, a common geometry for Zn(II) porphyrins.38 However, these exhibit the unique core structures commonly observed for antipodal β-substituted meso-tetraphenylporphyrinato metal complexes such as Ni(TPP(CN)₄)(L) (L = pyr or 1-meth).39 Fe(TPPBr₄)O,40 Fe(TPPBr₄)Cl₄, or Zn(TETTPP)(pyr)41 or Zn(TETTPP)(pyr) are M–N distances are nonequivalent in different N–N vectors (i.e., N₁–N₃ and N₂–N₄). The average Zn–N distances for 1b–3b along the N₁–N₃ vector (i.e., Zn–N in Table 2) are longer than those along the N₂–N₄ vector (i.e., Zn–N in Table 2). The nonequivalence of the M–N distances is caused by in-plane elongation of the porphyrin core due to the steric strain enforced by the

---


(43) Ni(TPP(CN)₄)(L): Hexacoordinate (2,3,12,13-tetracyano-5,10,15,20-tetraphenylporphyrinato)nickel(II). L = axial ligand. (a) Reference 19.

Inorganic Chemistry, Vol. 41, No. 25, 2002 6705
The mechanism of elongation of the porphyrin core is explained by repulsion of pyrrolic β-β substituents that push the meso-phenyl groups toward the unsubstituted pyrroles. Relief of the peripheral steric strain results in, for example, $C_{\beta}-C_{\beta'} > C_{\beta'}-C_{\beta}$ and $C_{\beta}-C_{meso}-C_{ph} > C_{a'}-C_{meso}-C_{ph}$, as shown in Table 2. This phenomenon is observed for 1b–3b, with 1b showing the largest elongation. The van der Waals radius of the trifluoromethyl group is estimated to be 2.2 Å (or more), which is larger than that of the methyl (2.0 Å) and the bromine groups (1.95 Å). Thus, of the three Zn(II) porphyrins, the strongest steric interaction among the peripheral substituents is expected in 1b. As suggested in previous reports, the electronic effect of β-substituents may also contribute to different $M-N$ distances in both vectors; strongly electron-withdrawing substituents on the pyrrolic β-positions will decrease the electron density on N1 and N3, and the weakened $M-N1$ and $M-N3$ bonds will be longer than the other $M-N$ pair.

Figure 1. X-ray crystal structures of (a) Zn(TPP(CF$_3$)$_4$)(EtOH)$_3$ (1b), (b) Zn(TPPBr$_4$)(MeOH)(DMF) (2b), and (c) Zn(TPP(CH$_3$)$_4$)(THF)$_1$CHCl$_3$$_{1.6}$ (3b). The axial ligand and the solvated molecules for the top views (left column) and the meso-phenyl groups and some solvated molecules for the side views (right column) were omitted for clarity. Ellipsoids are drawn at 30% probability.

Table 2. Core Size, Selected Bond Lengths (Å), Distances (Å), and Bond Angles (°)

|       | 1b     | 2b     | 3b     | Zn(TPP)  
|-------|--------|--------|--------|----------
| N···Ct | 2.106  | 2.094  | 2.076  | 2.043    
| N'···Ct | 1.962  | 2.009  | 2.012  |          
| Zn–O   | 2.110(3)| 2.108(3)| 2.182(4)| 2.228    
| Zn–N   | 2.119(2)| 2.115(3)| 2.092(5)| 2.050    
| Zn–N'  | 2.002(2)| 2.026(3)| 2.022(5)|          
| N–Cα   | 1.374(4)| 1.375(4)| 1.375(7)| 1.372    
| N–Cα'  | 1.381(4)| 1.370(4)| 1.377(7)|          
| Cα–Cβ  | 1.451(4)| 1.448(5)| 1.456(9)| 1.442    
| Cα'–Cβ' | 1.450(4) | 1.446(4) | 1.454(9) |          
| Cβ–Cβ'  | 1.368(4)| 1.350(5)| 1.370(9)|          
| Cβ'–Cβ'' | 1.336(4) | 1.344(5) | 1.348(8) |          
| Cα–Cmeso | 1.422(4) | 1.409(4) | 1.419(8) |          
| Cα'–Cmeso | 1.396(4) | 1.401(5) | 1.388(8) |          
| Cα–N–Cα'' | 108.2(2) | 108.2(3) | 105.9(5) | 106.8    
| Cα–N–Cα'' | 106.6(2) | 106.8(3) | 107.4(5) |          
| Cα–N–Cα'' | 106.6(3) | 107.9(3) | 112.6(2) | 117.2    
| Cα–N–Cα'' | 110.0(3) | 115.8(3) | 116.0(5) |          
| Cα–Cβ–X1(X4)' | 129.0(3) | 129.6(3) | 129.0(6) |          
| Cα–Cβ–X2(X3)' | 125.0(3) | 129.2(2) | 128.6(6) |          

a Reference 38.  b Ct is the centroid of the four nitrogen atoms.  c X1 = C21 or Br1, X2 = C22 or Br2, X3 = C23 or Br3, and X4 = C24 or Br4.

count to the conformaion of 1a, the major influence on the M–N distances results from the unique 18π-electron pathway. The free-base β-tetrakis(trifluoromethyl)-meso-tetraphenylporphyrin has a bacteriochlorin-like chromophore where the aromatic system avoids the CF3-substituted carbon atoms. 32 The crystal structure of (2,3,12,13-tetrahydro-5,10,15,20-tetraphenylporphino(pyridine)-zinc(II) 47 shows a similar core distortion with M–Ct is the centroid of the four nitrogen atoms. 3b is more or less the same as that in Zn(TPPBr4)2b, and a free base of a β-octafluoro-TPP analogue, H2TPPBr2, 3b shown planar porphyrin macrocycles. Thus, the distortion in 2b and Zn(TPPBr4)(H2O) seems due to the axial ligand coordination to the Zn(II) atoms. The average displacement of 0.46 Å for pyrrol β-carbons from the N4 mean plane in 3b is more or less the same as that in 2b and Zn(TPPBr4)(H2O), suggesting that the distortion in 3b could also be due to the coordination pattern of the Zn(II) atom and that the peripheral steric strain might not be sufficiently large to cause severe macrocyclic distortion. The obviously large average value of 0.79 Å for 1 indicates that factors other than the mode of coordination may be involved in the severe distortion of the macrocycle. Comparison of the root-mean-square values (Figure 2), which are the same as those in the least-squares plane, also shows the considerable distortion in 1b. The van der Waals radius of fluorine is close to that of hydrogen. 46 However, the larger C–F bond length (1.3–1.4 Å) compared to the C–H bond length (1.1 Å) 32 makes the CF3 group bulkier than the CH3 group. Thus, steric interactions among the peripheral substituents in 1b will be larger than those in 3b. As shown in the top view of 1b (Figure 1), two meso-phenyl groups are extremely twisted due to the steric interaction with trifluoromethyl groups. The average torsion angle made by Cnort1(C26 or C30)–C25–

much smaller than that of typical porphyrin ligands like TPP; the largest displacement of the Zn(II) atom in 1b corresponds to the smallest core size. The Zn–O distances in 1b and 2b are about 0.12 Å shorter than the 2.228 Å in Zn(TPP)(H2O)3b or 2.226 Å in Zn(OETPP)(MeOH)3b but close to that of (2.092 Å) in Zn(TPPBr4)(H2O). 34 Presumably, in electron-deficient porphyrins the Zn(II) atoms are pulled out of the porphyrin core by the axial ligand. Thus, the largest Zn(II) atom displacement in 1b is due to the combination of steric and electronic effects.

Figure 2 shows the magnitude of distortion in the macrocycles of 1b–3b. For all three, pyrrole rings are alternately up and down relative to the N4 mean plane. As shown in the displacements of the pyrrolic α-, β-, and meso-carbons, the pyrrole rings are slightly twisted along the M–N axes. Thus the macrocycles are mainly saddle-distorted and gently ruffled. The average displacements for the pyrrolic β-carbons from the N4 mean plane for 1b–3b are 0.79, 0.40, and 0.46 Å, respectively. Distortion of the macrocycles of 2b and 3b is similar to that in Zn(TPPBr4)(H2O), which is saddle-distorted and has a displacement of 0.49 Å for the pyrrolic β-carbons. 30 In fact, a potentially planar porphyrin can be distorted by the mode of coordination. For example, crystal structures of a four-coordinate Zn(TPPBr4) 31 and a free base of a β-octafluoro-TPP analogue, H2TPPBr2, 3b shown planar porphyrin macrocycles. Thus, the distortion in 2b and Zn(TPPBr4)(H2O) seems due to the axial ligand coordination to the Zn(II) atoms. The average displacement of 0.46 Å for pyrrol β-carbons from the N4 mean plane in 3b is more or less the same as that in 2b and Zn(TPPBr4)(H2O), suggesting that the distortion in 3b could also be due to the coordination pattern of the Zn(II) atom and that the peripheral steric strain might not be sufficiently large to cause severe macrocyclic distortion. The obviously large average value of 0.79 Å for 1 indicates that factors other than the mode of coordination may be involved in the severe distortion of the macrocycle. Comparison of the root-mean-square values (Figure 2), which are the same as those in the least-squares plane, also shows the considerable distortion in 1b. The van der Waals radius of fluorine is close to that of hydrogen. 46 However, the larger C–F bond length (1.3–1.4 Å) compared to the C–H bond length (1.1 Å) 32 makes the CF3 group bulkier than the CH3 group. Thus, steric interactions among the peripheral substituents in 1b will be larger than those in 3b. As shown in the top view of 1b (Figure 1), two meso-phenyl groups are extremely twisted due to the steric interaction with trifluoromethyl groups. The average torsion angle made by Cnort1(C26 or C30)–C25–

(50) Zn(TPPBr4)(H2O): Aqua(2,3,7,8,12,13,17,18-octafluoro-5,10,15,20-tetraphenylporphino(pyridine)-zinc(II). The value is the displacement from the porphyrin least-squares plane. Reference 14.
C5—C9(C4 or C6) is 54.4°, and similarly 52.1° for the other phenyl ring (C31—36). Interestingly, two other phenyl rings (C37—42 and C43—48) are almost orthogonal to the best plane of the porphyrin macrocycle (the corresponding torsion angles are 85.2° and 80.2°, respectively). The crystal structure of 1b viewed from a different angle (Figure 3) shows that the twisting angles of phenyl rings C25—30 and C31—36 affect those of phenyl rings C37—42 and C43—48. The steric interaction between phenyl ring C43—48 and trifluoromethyl group CF3 determines the orientation of the trifluoromethyl group CF1—3 because no fluorine of F1—3 is pointing at the face of the phenyl ring. This orientation forces F3 to point at the adjacent CF4—6, which orients so that F3 points between F4 and F5. The orientation of CF4—6 is such that the phenyl ring C25—30 cannot lie orthogonal to the porphyrinato core due to the penetration of F6 into the π-cloud of ring C25—30. In order to avoid this situation, the phenyl ring rotates to reduce the contact with CF4—6. The relatively small Cα—Cβ—X2 angle for 1b (Table 2) indicates that phenyl ring C25—30 is pushed away by CF4—6. Thus, an electrostatic repulsion between the π-cloud of the phenyl rings and the trifluoromethyl groups appears to be the major driving force for the macrocyclic distortion. Such interactions between fluorine atoms and the π-electrons of phenyl rings have been reported.54 It should be noted that the 282 MHz 19F NMR spectrum of 1b in CDCl3 at room temperature displayed a sharp singlet at −48.4 ppm (vs CFCl3), and this equivalency of the trifluoromethyl fluorines indicates rotation of the groups in solution.

The average torsion angles made by the Cortho—Cphen−

Figure 2. Displacements (in 0.01 Å units) of the porphyrin core, pyrrolic β-substituents, and Zn(II) atom relative to the N4 mean plane (left column) and linear display (in Å units) of the skeletal deviations from the N4 mean plane (right column) of (a) Zn(TPP(CF3)4)(EtOH)3 (1b), (b) Zn(TPPBr4)(MeOH)-(DMF)2 (2b), and (c) ZnTPP(CH3)4(TH0)1.6(CHClCl)0.4 (3b). ■ indicates the pyrrolic carbons bearing substituents. The rms values show the average deviation of the 24 core atoms from their least-squares plane.
trifluoromethyl groups where they are shielded by the ring current of the macrocycle. It is not possible that the intramolecular hydrogen bonding in 1b, shown in Figure 1, is the rationale for the mode of buckling, since we also observed similar coordination and distortion patterns for a crystal structure of CoII(TPP(CF3)4)(pyr),5,10,15,20-tetraphenylporphyrinato)cobalt(II). Source for the redox potentials of Zn(TPP(CN)4): Giraudou, A.; Callot, H. J.; Gross, M. Inorg. Chem. 1979, 18, 201. (58) σp values for the substituents were obtained from ref 58a. See ref 58b for the redox potentials vs σp values. (a) Hansch, C.; Leo, A.; Taft, R. W. Chem. Rev. 1991, 91, 165. (b) Kadish, K. M.; Morrison, M. M. J. Am. Chem. Soc. 1976, 98, 3326.

Optical Spectra. Figure 4 shows the optical spectra of 1a–3a. 3a shows a spectrum similar to that of Zn(TPP) (419, 548, and 582 nm), while 2a shows a small red shift. Compound 1a, on the other hand, exhibits a unique optical spectrum. The extremely red-shifted Q-band is indicative of a narrower HOMO–LUMO, see below, which is caused by both the macrocyclic distortion4 and the bacteriochlorin-like electronic structure.32 It is interesting to note that [meso-tetrakis(trifluoromethyl)porphyrinato]zinc(II) (λmax, nm (log ε) 409 (5.27), 554 (3.39), 593 (4.29),27 where the four CF3 groups are bonded to the meso positions, exhibits an optical spectrum27 similar to that of Zn(TPP).

Redox Potentials of Zn(II) Porphyrins. In the previous section, the relationship between the optical properties and structures was described briefly. In addition, we have also attempted to analyze the electronic structures of the Zn(II) porphyrins using cyclic voltammetry. Cyclic voltammetric measurements were performed using the four-coordinate complexes Zn(TPP(CF3)4) (1a), Zn(TPPBr4) (2a), and Zn(TPP(CH3)4) (3a). As presented in Figure 5a, two reversible one-electron waves were observed for 1a. The first oxidation and reduction potentials of 1a (β-CF3), 2a (β-Br), 3a (β-CH3), Zn(TPP) (β-H), and Zn(TPP(CN)4)57 (β-CN) are plotted against the 4σp value (Figure 5b).58 As the 4σp value increases, both the oxidation (removal of an electron from the HOMO) and reduction (filling of an electron into the LUMO) potentials increase. The first oxidation potentials change almost linearly. A slight deviation of the first (55) Scheidt, W. R. In The Porphyrins; Dolphin, D., Ed.; Academic Press: New York, 1978; p 463.
The HOMO–LUMO gap contraction is also unlikely in the four-coordinate Zn(TPP(CN)₄). Thus, the HOMO–LUMO gap contraction should be mainly related to the electronic effect of the β-substituents. In a recent report, we demonstrated that a dramatic HOMO–LUMO gap contraction is observed for the free bases of β-trifluoromethyl-meso-tetraphenylporphyrins with a fixed 18ξ-electron pathway. Thus, the large HOMO–LUMO gap contraction in 1a presumably originates from its unique electronic structure. In β-octasubstituted porphyrins the electronic effect of peripheral substituents does not normally affect the HOMO–LUMO gap whereas macrocyclic distortion does. It should be noted that the gap contraction observed for the antipodally β-substituted electron-deficient porphyrins such as 1a or Zn(TPP(CN)₄) is significantly larger (> 600 mV) when compared to an offset by severe macrocyclic distortion (< 500 mV for Zn(II) complexes of β-octabromoporphyrins). It also should be noted that the HOMO–LUMO gap of [meso-tetakis(trifluoromethyl)porphyrinato]zinc(II) (Zn(P(CF₃)₄)) has been reported as 2.15 V (in benzonitrile), which is similar to that of Zn(TPP). The large difference between 1a and Zn(P(CF₃)₄) indicates that the position of the groups affects the HOMO–LUMO gap greatly. The electronic effect of the groups in 3a is not significant.

**Conclusion**

A comparative analysis of the structures of three 2,3,12,-13-tetrasubstituted porphyrins determined by X-ray crystallography revealed that the electronic and steric effects of pyrrolic β-trifluoromethyl groups on the macrocycle are dramatic. Steric interactions between the trifluoromethyl and phenyl groups and the strong electron-withdrawing effect of the trifluoromethyl groups are the driving force for the severe macrocycle in-plane and out-of-plane distortions. The electronic structure, specifically of 1a, also reveals the dramatic effects of the β-trifluoromethyl substitution where, as with the free base, the 18ξ-aromatic system is locked and avoids the atoms bearing these groups.

**Acknowledgment.** We thank Prof. Brian James and his group in the Department of Chemistry at the University of British Columbia for their generous support of the cyclic voltammetric measurements. This work was supported by the Natural Science and Engineering Research Council of Canada.

**Supporting Information Available:** Table of redox potentials of 1a–3a. X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org. IC020339H

---