2,3,7,8,12,13,17,18-Octafluoro-5,10,15,20-tetraphenylporphyrin: First Synthesis and X-Ray Crystal Structure of the Zn^{II} Complex

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Abstract: 2,3,7,8,12,13,17,18-Octafluoro-5,10,15,20-tetraphenylporphyrin has been prepared from 3,4-difluoropyrrole and benzaldehyde under Lindsey conditions. An X-ray crystal structure study of its Zn^{II} complex has shown that the macrocycle core is nonplanar, a result in apparent contradiction with a blue-shifted UV/Vis spectrum. The results reported here demonstrate that a wide range of β-octafluoro-*meso*-arylated porphyrins, a new class of highly electron-deficient ligands, are potentially accessible from 3,4-difluoropyrrole, thus opening the door to, inter alia, efficient and robust oxidation catalysts.

Keywords
heterocycles · fluorine · porphyrinoids · zinc

Introduction

Haloporphyrins and their metal derivatives have spurred a growing interest during the last few years owing to their excellent catalytic properties including robustness and efficiency. While the observed effects, for example, in metalloporphyrin-catalyzed oxygenation reactions, have resulted mainly from the presence of electron-withdrawing substituents in the β-positions, it has been shown that steric factors due to *meso* or β-substitution could also markedly affect the porphyrin properties by distorting the macrocycle.[1, 2]

So far, most of these studies have been confined to various β-polybromo- or β-polychloroporphyrins[2] prepared by direct halogenation of the parent porphyrin or a metal derivative with the corresponding *N*-halosuccinimide[2a–e, q] or occasionally with bromine,[2f] chlorine,[2g] or phenylselenyl halides.[2h]

Primarily due to the lack of convenient synthetic routes, only two examples of β-fluoroporphyrin syntheses have been reported to date. In the first, Ogoshi et al. prepared 2,7,12,17-tetrafluoro-3,8,13,18-tetramethylporphyrin in 2% yield by tetramerization of 4-fluoro-5-hydroxymethyl-3-methylpyrrole-2-carboxylic acid.[3] In the second, it was claimed that 2,3,7,8,12,13,17,18-octafluoro-5,10,15,20-tetrakis(pentafluorophenyl)porphyrin ($F_{28}TPPH_2$) had been prepared by direct fluorination of the parent metalated porphyrin ($F_{20}TPPZn$) with silver or cobalt fluorides,[4] or with fluorine combined with small amounts of one of these fluorides.[5] Unfortunately, full characterization data were not available from the reports on F_{28} fluoroporphyrins, which are mainly confined to the patent literature. In an alternative approach to these promising ligands, we sought to elaborate the octafluoroporphyrin macrocycle from a fluorinated pyrrole unit.

Results and Discussion

As an attempted synthesis of the parent 2,3,7,8,12,13,17,18-octafluoroporphyrin (OFP) from 3,4-difluoro-2-(hydroxymethyl)pyrrole failed,[6] we came to use 3,4-difluoropyrrole (**1**) as the starting material in a route to 2,3,7,8,12,13,17,18-octafluoro-5,10,15,20-tetraphenylporphyrin (**2**), selected as a model. For this purpose, the final step of our previously described preparation of **1**, that is, decarboxylation of 3,4-difluoropyrrole-2-carboxylic acid in quinoline in the presence of barium-promoted copper chromite,[7] proved to be unsatisfactory. In a reexamination of this crucial step, the classical "dry" decarboxylation over copper powder afforded 3,4-difluoropyrrole (**1**) in 70–80% yield.

Whereas the protocol of Treibs and Häberle (**1**, PhCHO, HOAc/pyridine, air)[8] failed to produce any trace of porphyrin **2**, 3,4-difluoropyrrole (**1**) was found to react "normally" (compared with pyrrole) with benzaldehyde under Lindsey conditions,[9] to give the intermediate β-octafluoro-*meso*-tetraphenylporphyrinogen (identified by mass spectrometry). Subsequent oxidation of the porphyrinogen with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) afforded the desired 2,3,7,8,12,13,17,18-octafluoro-5,10,15,20-tetraphenylporphyrin (β-F_8TPPH_2) (**2**). Isolation of the free ligand was preferably

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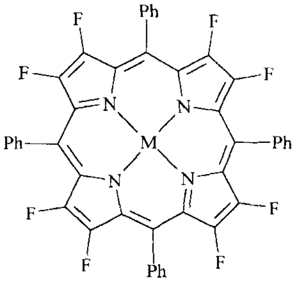

2, M = 2H
3, M = Zn

achieved by prior formation of its zinc(II) complex **3** (β-F_8TPPZn) with zinc acetate in methanol and purification of this complex by column chromatography. Subsequent quantitative demetalation of **3** with trifluoroacetic acid via the (green) diprotonated form of **2**, β-$F_8TPPH_4^{2+}$, afforded the free ligand **2** in a yield of up to 40%.

The structures of **2** and **3** were established unambiguously by UV/Vis spectroscopy, ^{13}C, ^{1}H, and ^{19}F NMR spectroscopy, mass spectrometry, and by an X-ray crystal structure analysis for **3**.

A remarkable feature for porphyrins **2** and **3** appears in their electronic absorption spectra, which show a systematic 12–18 nm hypsochromic shift compared with those of *meso*-tetraphenylporphyrin ($TPPH_2$) and its Zn^{II} complex (TPPZn) (Table 1). For example, the Soret (B) absorption band of **2** was found at 404 nm (cf. 419 nm for the analogous transition of $TPPH_2$), while that of **3** was found at 410 nm (cf. 427 nm for TPPZn). In contrast, the Soret and Q bands of 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenylporphyrin exhibit a large red-shift of approximately 6 nm, with respect to the bands observed for $TPPH_2$, for each bromine atom introduced.[2f] This effect, first pointed out by Callot for β-bromoporphyrins,[2a] was attributed mainly to the saddle-shaped conformation adopted by the molecule, a consequence of van der Waals repulsion between the *meso* and β substituents.[2k, 10] The same trend was observed for β-octachloro-*meso*-tetraphenylporphyrin with a Soret band at 452 nm.[11] A comparison of the UV/Vis spectra of **2** and **3** with those of the two related structures reported to date was not conclusive with respect to the unusual blue-shift observed. The Soret band of 2,7,12,17-tetrafluoro-3,8,13,18-tetramethylporphyrin was found at 387 nm,[3] while that for β-octamethylporphyrin was at 398 nm;[12] the Q bands were also blue-shifted. As these two porphyrins are free of π or steric interactions due to substituents at the *meso* positions, the observed hypsochromic shift for the tetrafluoroporphyrin can be interpreted as a direct effect of the electronegativity of fluorine. In contrast, the Soret absorption band of $F_{28}TPPH_2$ has been reported at 430 nm, which is red-shifted relative to the 411 nm for the 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin ligand ($F_{20}TPPH_2$) (also, 441 nm for F_{28}TPPZn vs. 417 nm for F_{20}TPPZn).[4, 13]

Table 1. UV/Vis data for fluoroporphyrins **2** and **3** and their hydrogen-substituted analogues [a,b].

Compound	Soret	Q bands			
β-F_8TPPH_2 (**2**)	404 (164400)	500 (13100)	534 (4700)	581 (3200)	637 (3300)
β-F_8TPPZn (**3**)	410 (336000)	540 (17100)	577 (5600)		
$TPPH_2$	419	516	550	593	651
TPPZn	427	556	595		

[a] λ_{max} [nm]. [b] In chloroform.

The ^{19}F NMR spectrum of the sparingly soluble free-base **2** in $CDCl_3$ was also unusual. At 293 K, two very broad signals ($\Delta\nu \approx 1548$ Hz at 282 MHz) were observed, attributable to two types of fluorine nuclei in slow exchange on the NMR time scale. On heating, coalescence was reached at approximately 313 K. Above this temperature the signal sharpened as the fluorine atoms became equivalent on the NMR time scale. The free energy of activation $\Delta G^{\neq}$ for the observed dynamic process, identified as NH tautomerism, was calculated at the coalescence temperature as 13.3 kcal mol^{-1},[14] which compares well with the value reported for NH tautomerism in $TPPH_2$ (12.3 kcal mol^{-1}; 303 K, ^{13}C NMR)[15] and in 2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetraphenylporphyrin ($OETPPH_2$) (13.7 kcal mol^{-1}; 293 K, ^{1}H NMR).[16] In contrast, the ^{19}F NMR spectrum of the metalated porphyrin **3** appears as a sharp singlet.

A single crystal of **3**, suitable for X-ray diffraction analysis, was obtained as the acetone solvate by slow evaporation of an acetone solution; in addition a molecule of water was bound to the zinc atom. The porphyrin core of **3** was found to be nonplanar, displaying essentially a pronounced saddle shape (see Figure 1), like the zinc(II) complexes of β-octaethyl- and β-octamethyl-*meso*-tetraphenylporphyrins (which crystallized as the methanol and pyridine adducts, respectively)[16] or β-octabromo-*meso*-tetraarylated porphyrins in their free-base form[17a] or complexed with zinc(II),[17b, 18a] nickel(II),[2k, 18b] or copper(II).[18b]

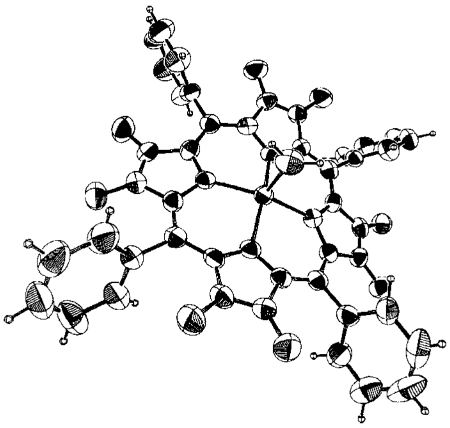

Figure 1. Molecular structure of β-F_8TPPZn (**3**) (thermal ellipsoids at the 50% probability level).

As shown in Figure 2, the pyrrole rings are tilted alternately upwards and downwards relative to the mean porphyrin plane; the macrocycle core is also gently ruffled (S_4-distorted) with a maximum displacement of 0.13 Å for the C_{meso} atoms and 0.59 Å for the C_β atoms.[19] In contrast, all atoms of the macrocycle core of the five-coordinate adduct (5,10,15,20-tetraphenyl-

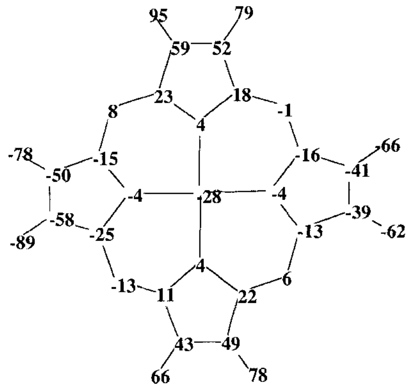

Figure 2. Diagrammatic representation of the porphyrin core of β-F_8TPPZn (3), illustrating the extent of the macrocycle distortion in units of 0.01 Å.

porphinato)Zn^{II}·H_2O (TPPZn·H_2O) are coplanar.[20] The zinc atom of **3** is displaced axially from the porphyrin least-squares plane from 0.28 Å (cf. 0.173 Å for TPPZn·H_2O[21] and 0.22 Å for OETPPZn·MeOH[16f]). The average Zn–N distance of 2.068(5) Å is typical of five-coordinate Zn porphyrins.[20] Nevertheless, the Zn–O distance of 2.092(5) Å is significantly shorter than that found, for example, in TPPZn·H_2O (2.228 Å)[20] or OETPPZn·MeOH [2.226(5) Å].[16f] This shortening may be regarded as an effect of the fluorine electronegativity.

It is now established that structural changes in porphyrins have a dramatic electronic effect by modulation of the HOMO–LUMO energy gap. While the bathochromic shifts observed in the optical spectra of porphyrins, for example, β-Br_8TPPH_2,[2f] have been considered to be intrinsic to ring distortion, recent studies on nonplanar dodecaalkylporphyrins[19c] and *meso*-(perfluoroalkyl)porphyrins[21] have suggested that these shifts originate from core conformations *and* substituent effects. Although the conformation in solution of porphyrin **3** has not been determined to date, we suppose that the unprecedented hypsochromic shift observed in its UV/Vis absorption spectrum is merely a consequence of the strong overall electron-withdrawing effect of the eight fluorine atoms completely offsetting a (possible) bathochromic shift due to macrocycle distortion.

Conclusion

It has been shown for the first time that β-octafluoroporphyrins can be obtained from 3,4-difluoropyrrole, the reactivity of which appears to be unexpectedly close to that of pyrrole itself. Further studies on the properties of these porphyrins and others are underway, including their redox behavior and catalytic activity.

Experimental Section

2,3,7,8,12,13,17,18-Octafluoro-5,10,15,20-tetraphenylporphyrin (β-F_8TPPH_2, 2) and its Zn^{II} complex (β-F_8TPPZn, 3): Boron trifluoride diethyl etherate (30 µL) was added in one portion to a stirred solution of pyrrole **1** (76 mg, 0.745 mmol) and freshly distilled benzaldehyde (79 mg, 0.745 mmol) in anhydrous CH_2Cl_2 (74 mL) under argon. Stirring was continued for 1 h, and DDQ (127 mg, 0.559 mmol) was added in one portion. After 1 h of additional stirring, the mixture was concentrated. The residue was filtered off and washed with methanol to afford 66 mg of crude **2**. The product was dissolved in CH_2Cl_2 (100 mL) and stirred overnight with 2 mL of a saturated solution of zinc acetate in methanol (UV/Vis monitoring). After concentration, column chromatography (silica gel, CH_2Cl_2) afforded **3** as red microcrystals. Yield: 66 mg (43%). Quantitative demetalation was performed with trifluoroacetic acid, affording **2** as brownish microcrystals.

2: ^{1}H NMR (500.13 MHz, $CDCl_3$): $\delta = -4.19$ (s, 2H, NH), 7.66 (t, 8H, *m*-H), 7.72 (t, 4H, *p*-H), 8.00 (d, 8H, *o*-H); ^{19}F NMR (282.4 MHz, $CDCl_3$): $\delta = -140.9$ (vbrs, 4F), -146.4 (vbrs, 4F); high-resolution MS (EI) ($C_{44}H_{22}F_8N_4$): calcd 758.1716, found 758.1708.

3: ^{1}H NMR (500.13 MHz, $CDCl_3$): $\delta = 7.69$ (t, 8H, *m*-H), 7.75 (t, 4H, *p*-H), 8.0 (d, 8H, *o*-H); ^{19}F NMR (235.35 MHz, $CDCl_3$): $\delta = -143.3$ (s); ^{13}C NMR (125.75 MHz, $CDCl_3/CD_3OD$): $\delta = 118.42$ (s, *meso*-C), 126.92 (s, *m*-C_{phe}), 128.21 (s, *p*-C_{phe}), 131.77 (s, *o*-C_{phe}), 133.61 (m, α-C), 138.30 (s, *ipso*-C), 146.28 (dd, $J = 275.0$, 10.1 Hz, β-C); high-resolution MS (FAB, 3-nitrobenzyl alcohol/glycerol matrix) ($C_{44}H_{20}F_8N_4Zn$): calcd 820.0851; found 820.0848.

Crystal structure analysis for 3·H_2O·C_3H_6O: $C_{47}H_{28}F_8N_4O_2Zn$, $M_r = 898.13$. Crystal dimensions: 0.35 × 0.40 × 0.40 mm, deep purple, monoclinic, space group $P2_1/c$, $a = 14.504(9)$, $b = 13.476(9)$, $c = 22.502(5)$ Å, $\beta = 91.36(4)°$, $V = 4397(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.390$ g cm^{-3}, $\mu = 6.436$ cm^{-1}, $F(000) = 1824$. Diffractometer: CAD4 Enraf-Nonius, graphite monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.70926$ Å), $T = 293$ K. Program: MOLEN Enraf-Nonius.[22] Measurements details: the cell parameters were obtained by fitting a set of 25 high-theta reflections. The data collection [$2\theta_{max} = 50°$, scan $\omega/2\theta = 1$, $t_{max} = 60$ s; range of *hkl*: $h = -26$ to 26, $k = 0$ to 16, $l = 0$ to 17; intensity controls without appreciable decay (1.3%)] gave 8396 reflections of which 3247 were independent ($R_{int} = 0.038$) with $I > 3\sigma(I)$. After Lorentz and polarization corrections, the structure was solved by direct methods revealing the Zn and N atoms. The remaining non-hydrogen atoms were found after successive scale factor refinements and Fourier differences. After isotropic ($R = 0.105$), then anisotropic refinement ($R = 0.095$), two groups of some disordered atoms were found (acetone molecules) and the hydrogen atoms located with a Fourier difference (between 0.57 and 0.23 e Å^{-3}). The whole structure was refined by the full-matrix least-squares techniques (use of F magnitude; x, y, z, β_{ij} for Zn, N, C, and O atoms and x, y, z for H atoms, solvent atoms refined with B_{iso}; 632 variables and 3247 observations; $w = 1/\sigma(F_o)^2 = [\sigma^2(I) + (0.04\,F_o^2)^2]^{-1/2}$) with the resulting $R = 0.054$, $R_w = 0.050$ and $S_w = 1.44$ (residual $\Delta\rho \leq 0.26$ e Å^{-3}). Atomic scattering factors came from ref. [23]. The multiplicity of acetone molecules was estimated at approximately 0.5. In the second group of atoms, it was not possible to assign the oxygen atom unambiguously. Under these conditions, the formula was assumed to be $C_{44}H_{22}F_8N_4OZn \cdot C_3H_6O$.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100203. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: Int. code +(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk).

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