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Synthesis and Structure of 16 π Octaalkyltetraphenylporphyrins

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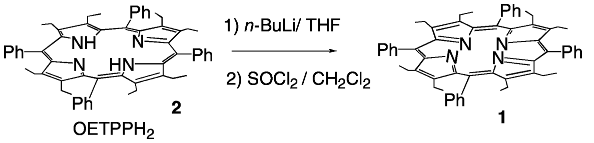
Porphyrin with a stable aromatic 18 π electron core has been widely studied mainly due to its biological functions[1] and its coordinating ability toward most transition metals and main group elements.[2] Although there have been several reports on nonaromatic "expanded" porphyrin analogues,[3] 16 π electron porphyrins with the same but oxidized porphyrin skeleton have never been reported so far. We now report the isolation and X-ray structural characterization of the two 16 π electron octaethyl- and octaisobutyltetraphenylporphyrins (**1** and **3**, respectively).

Scheme 1. Synthesis of the Oxidized OETPP (**1**)



During our investigation of the main group element hypervalent compounds[4] and porphyrins,[5] we accidentally found that the oxidized octaethyltetraphenylporphyrin (OETPP, **1**) could be isolated from the reaction of OETPPLi$_2$ with SOCl$_2$ (Scheme 1).[6] The precise X-ray analysis of **1** revealed all the hydrogen atoms in **1**, but there are no N−H hydrogens and even no central atom (Figure 1).[7]

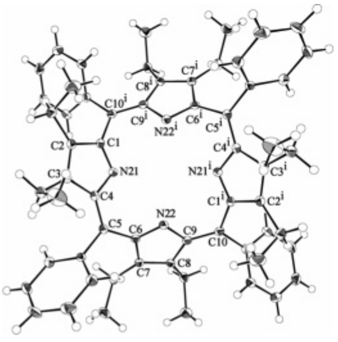


Figure 1. ORTEP drawing of **1** (50% probability ellipsoid) with two molecules of CH$_2$Cl$_2$ omitted for clarity.

The porphyrin skeleton of **1** was much more distorted from the mean plane of the porphyrin core than that of the parent OETPPH$_2$ (**2**), as shown in Figure 2. The figures show the deviations (in units of 0.01 Å) of the skeletal atoms from the mean plane defined by the 24 core atoms of the porphyrin.[8] The degree of distortion of the core, which can be evaluated by the root-mean-square of the sum of squares of the deviation of each atom from the mean plane, was calculated to be 0.836 for **1** in comparison with 0.712 for **2**.

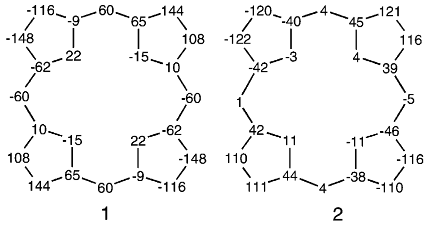


Figure 2. Deviation of each atom from the mean plane (in units of 0.01 Å) in the molecular structure of OETPP (**1**) and OETPPH$_2$ (**2**).

In addition, a clear bond alternation was observed among a single and a double bond of C−C and C−N bond in the 16 π system of **1**, as shown in Figure 3, which contrasts with aromatic the 18 π system of **2**.

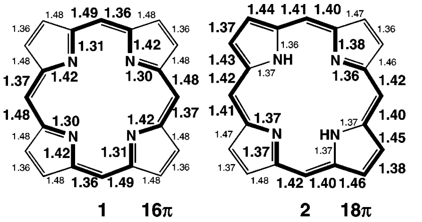


Figure 3. Bond alternation (in Å) in the porphyrin cores of **1** in contrast to **2**.

The UV−vis spectra of **1** are also quite characteristic. The Soret band is shifted to a much shorter wavelength when compared with that of **2**, and the Q-bands are not observed in **1** {λ_{max} (log ϵ) **1**: 275 (4.52), 339 (4.78); **2**: 446 (5.20), 548 (4.28), 588 (4.23)}. Since the definite bond alternation and the unique UV−vis spectra are quite consistent with the recently reported $[4n] - \pi$ electronic (28 π, 32 π, 36 π) porphyrinoids,[9] **1** should be the first example of a 16 π nonaromatic porphyrin.

Although **1** is not quite stable in solution, especially in polar solvents, such as acetonitrile, **1** was relatively stable in CH$_2$Cl$_2$ in a refrigerator (−4 °C). It should be pointed out here that in the crystal lattice of **1** there are two molecules of CH$_2$Cl$_2$, and one of them is disordered (whose hydrogen are suitably positioned for hydrogen bonding with the nitrogen of the pyrrole), while the other is suitably positioned for the CH/π interaction with the two pyrrole

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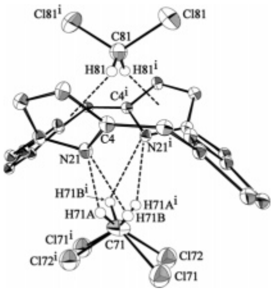

Figure 4. CH/π interaction between one of the dichloromethane molecules with the pyrrole moiety in **1**.

rings (Figure 4). The distance between the carbon atom of CH_2Cl_2 and the mean plane of the pyrrole ring is 3.53 Å. Therefore, we calculated the stabilizing energy by the CH/π interaction of CH_2Cl_2 with a pyrrole at the MP2/cc-pVTZ level calculation. Although, the CH/π interaction between the relatively acidic hydrogen in CH_2Cl_2 with benzene has already been reported to be mainly due to a dispersion interaction, together with a Coulomb interaction, and the stabilization energy was calculated to be 4.5 kcal/mol.[10] The stabilization energy of CH_2Cl_2 with a pyrrole is even higher at 5.7 kcal/mol. Since two CH/π interactions of this type exist in **1**, the stabilizing energy by CH_2Cl_2 should be much larger. It should be noted that the calculated distance (3.23 Å) between the carbon atom of CH_2Cl_2 and the mean plane of the pyrrole ring is quite consistent with the distance from the precise X-ray analysis.

Although the mechanism of formation of **1** has not yet been clarified, the cheletropic reaction of the unstable OETPPS(═O) may take place. However, it is clear that the relatively easy oxidation of the parent porphyrin took place in **2**. We believe that the nonplanarity of **2** caused by the steric congestion with spherical substituents should be the decisive factor to give **1**, even though **1** is not very stable. Therefore, to obtain a more stable 16 π oxidized porphyrin, the more sterically congested octa*iso*butyltetraphenylporphyrin (O*iso*BuTPPH$_2$, **4**)[11] was synthesized from 3,4-di*iso*butylpyrrole.[12] Fortunately, the expected oxidized O*iso*BuTPP (**3**) was obtained using similar procedures. The UV−vis spectra of **3** were similar to those of **1**, although the absorption maxima slightly shifted to a shorter wavelength {λ_{max} **3**: 274, 330.5}. The X-ray analysis of **3** showed a very similar distorted nonplanar structure to that of **1**, but in this case, H_2O was found in the center of the core instead of CH_2Cl_2 (see Supporting Information).[13] Therefore, in **3**, the hydrogen bond interaction stabilizes **3** instead of the CH/π interaction in **1**. Although **3** is somewhat more stable than **1**, as expected, the complexation of **3** with some transition metals has not yet been successful. The evaluation of using **1** or **3** as a bidentate ligand for transition metals and the preparation of more sterically congested octaalkyltetraarylporphyrins are now in progress.

Supporting Information Available: Preparation and spectral data of **3** and **4**, procedure of X-ray measurements, and cif data of **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) **Synthesis of 1**: To a solution of **2** (500 mg, 0.596 mmol) in dry THF (40 mL) was added *n*-butyllithium (1.5 M solution in *n*-hexane, 0.80 mL, 1.19 mmol) under N_2. The solution was stirred for 3 h at room temperature. After removal of the solvent in vacuo, the residue was redissolved in CH_2Cl_2 (40 mL). To the solution was added freshly distilled thionyl chloride (0.045 mL, 0.596 mmol). The reaction mixture was then stirred for 1 day at room temperature. After removal of the solvent, the residue was subjected to neutral alumina column chromatography (Brockman grade III, CH_2Cl_2). **1** could be isolated (188.0 mg, 31.9%) as the second brown fraction with partial decomposition during chromatography. The product was recrystallized from CH_2Cl_2/*n*-hexane in a refrigerator (−4 °C). ^{1}H NMR (δ, $CDCl_3$): 0.62 (t, 12H, $J = 7$ Hz), 0.71 (t, 12H, $J = 7$ Hz), 1.66 (sext, 4H, $J = 7$ Hz), 1.82 (sext, 4H, $J = 7.3$ Hz), 2.02−2.11 (m, 8H), 4.25 (br s, 2H), 7.28−7.50 (m, 20H). UV−vis (CH_2Cl_2) λ_{max} (log ϵ): 275 (4.52), 339 (4.78). Mp 279−281 °C (dec).

(7) Crystal data of **1** + 2CH_2Cl_2: $C_{62}H_{64}Cl_4N_4$, $M = 1006.97$, monoclinic, space group $C2/c$, $a = 28.0983(9)$ Å, $b = 12.0933(5)$ Å, $c = 19.9538(7)$ Å, $\beta = 128.477(1)°$, $U = 5308.0(3)$ Å^3, $Z = 4$, $D_c = 1.260$ g cm^{-3}, $T = 100$ K. Data were collected on an automated imaging plate Weissenberg camera, Rigaku Raxis-Rapid, using Mo Kα radiation ($\lambda = 0.710$ 73 Å) generated from a fine focus sealed tube by an oscillation method at 100 K. Final $R = 0.0521$ ($Rw = 0.1393$) for 6009 observed reflections with $I > 2\sigma(I)$.

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(11) **Synthesis of 4 and 3**: Octa*iso*butyltetraphenylporphyrin (O*iso*BuTPPH$_2$, **4**) was prepared by the reaction of 3,4-di*iso*butylpyrrole and benzaldehyde in the presence of a catalytic amount of boron trifluoride diethyl etherate and oxidation by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). Yield 31%. ^{1}H NMR (δ, $CDCl_3$): 0.07−0.17 (m, 24H), 0.37−0.51 (m, 24H), 1.08−1.26 (m, 8H), 1.89−2.27 (m, 16H), 7.80−7.82 (m, 12H), 8.38−8.40 (m, 8H). UV−vis (CH_2Cl_2), λ_{max}: 357, 465, 563, 617, 723. O*iso*BTPP (**3**) was synthesized based on the similar procedures for the preparation of **1**. ^{1}H NMR (δ, $CDCl_3$): 0.46 (d, 12H, $J = 7$ Hz), 0.59 (d, 12H, $J = 7$ Hz), 0.77 (d, 12H, $J = 7$ Hz), 0.82 (d, 12H, $J = 7$ Hz), 1.27−1.30 (m, 8H), 1.62−1.75 (m, 10H), 1.95−2.07 (m, 6H), 7.37−7.43 (m, 20H). UV−vis (CH_2Cl_2), λ_{max}: 274, 330.5.

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(13) Crystal data of **3** + H_2O: $C_{76}H_{96}N_4O$, $M = 1097.60$, tetragonal, space group $I4_1/a$, $a = 18.0480(3)$ Å, $c = 25.8620(6)$ Å, $U = 8424.0(3)$ Å^3, $Z = 6$, $D_c = 1.277$ g cm^{-3}, $T = 200$ K. Mo Kα radiation (λ=0.710 73 Å). Final $R = 0.104$ ($Rw = 0.199$) for 3514 observed reflections with $I > 3\sigma(I)$.

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