Crystal Structure of a Remarkably Ruffled Nonplanar Porphyrin (Pyridine)[5,10,15,20-Tetra(tert-butyl)porphyrinato]zinc(ii)

Mathias O. Senge,*† Tadashi Ema and Kevin M. Smith*
Department of Chemistry, University of California, Davis, CA 95616, USA

The title compound presents the first example of a sterically ruffled porphyrin bearing only meso substituents; the degree of ruffling is severe, with C_m displacements of up to 1 Å.

Recent synthetic and structural studies on porphyrins have concentrated on investigations of porphyrin nonplanarity induced by peripheral steric strain. Examples of conformationally designed porphyrins, specifically synthesized to yield porphyrins with nonplanar macrocyclic conformations and whose structures have been determined by X-ray crystallography are octaethyltetraphenylporphyrin (H_2OETPP),^2 dodecapropylporphyrin,^3 octahalogenotetrapyrrins,^4 octaethyltetraphenylporphyrin^5 and tetracycloalkenyltetraphenylporphyrins. All these compounds exhibit striking spectroscopic characteristics inferred a distorted macrocyclic conformation for compounds like 5,10,15,20-tetra(tert-butyl)porphyrin (H_2TtBuP).^7

While nonplanar porphyrins such as H_2OETPP undergo metallation and protonation reactions in a manner similar to that of their planar counterparts, H_2TtBuP yielded porphodimethenes. Indeed, the difference in reactivity between H_2TtBuP and H_2OETPP was taken as an indication that the former might even be more distorted (both in solution and in the solid state) than are H_2OETPP and its derivatives.

Using mild and brief reaction conditions for the metallation of H_2TtBuP, we have prepared a variety of metal complexes and obtained crystals of the pyridine adduct of Zn^{II}TtBuP suitable for a crystallographic structure determination. Fig. 1 shows the molecular structure in the crystal and gives some selected structural data. The illustration clearly indicates a nonplanar macrocyclic conformation. Surprisingly, the macrocyclic conformation is ruffled significantly as indicated by the tilt of the pyrrole planes against each other (36°) and the alternating up and down displacement of the C_m positions. Individual pyrrole rings are tilted on average by 26.3° from the 4N plane. This is in contrast to the nonplanar structures of dodecasubstituted free-base and zinc(ii) porphyrins^1−6 which so far have been shown to possess mostly saddle distortion. Ruffled conformations have been found e.g. in Ni^{II} porphyrins, where the small metal ion induces ruffling owing to Ni-N bond shortening. A strongly nonplanar ruffled conformation has also been found in the dodecasubstituted Ni^{II} complex of 2,3,7,8,12,13,17,18-tetracyclopentenyl-5,10,15,20-tetra-n-pentylporphyrin (H_2TC_5TPnP) and it was suggested by molecular mechanics calculations that interaction of the methylene hydrogens of the CH_2 group bound to the C_m position with the β-pyrole substituents is responsible for the observed nonplanarity. The present structure shows that the presence of a bulky meso substituent alone (and its interaction with the β-pyrole hydrogens) can lead to even more distorted macrocycles. Fig. 2 presents the deviations of the macrocycle atoms from the 4N plane. The meso hydrogens show the largest deviations from planarity (average deviation 0.899 Å) and the average deviation of H_2TtBuP, we have prepared a variety of metal complexes and obtained crystals of the pyridine adduct of Zn^{II}TtBuP suitable for a crystallographic structure determination.† Fig. 1 shows the molecular structure in the crystal and gives some selected structural data. The illustration clearly indicates a nonplanar macrocyclic conformation. Surprisingly, the macrocyclic conformation is ruffled significantly as indicated by the tilt of the pyrrole planes against each other (36°) and the alternating up and down displacement of the C_m positions. Individual pyrrole rings are tilted on average by 26.3° from the 4N plane. This is in contrast to the nonplanar structures of dodecasubstituted free-base and zinc(ii) porphyrins^1−6 which so far have been shown to possess mostly saddle distortion. Ruffled conformations have been found e.g. in Ni^{II} porphyrins, where the small metal ion induces ruffling owing to Ni-N bond shortening. A strongly nonplanar ruffled conformation has also been found in the dodecasubstituted Ni^{II} complex of 2,3,7,8,12,13,17,18-tetracyclopentenyl-5,10,15,20-tetra-n-pentylporphyrin (H_2TC_5TPnP) and it was suggested by molecular mechanics calculations that interaction of the methylene hydrogens of the CH_2 group bound to the C_m position with the β-pyrole substituents is responsible for the observed nonplanarity. The present structure shows that the presence of a bulky meso substituent alone (and its interaction with the β-pyrole hydrogens) can lead to even more distorted macrocycles. Fig. 2 presents the deviations of the macrocycle atoms from the 4N plane. The meso hydrogens show the largest deviations from planarity (average deviation 0.899 Å) and the average deviation

Fig. 1 View of the molecular structure of Zn^{II}TtBuP(pyr) in the crystal. Thermal ellipsoids are drawn for 50% occupancy; hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Zn−N(1A) 2.165(4), Zn−N(21) 2.0245(5), Zn−N(22) 2.0100(6), Zn−N(23) 2.010(5), Zn−N(24) 2.0065(5), C(5)−C(1) 1.555(7), C(10)−C(11) 1.555(7), C(11)−C(12) 1.555(7), C(12)−C(13) 1.555(7), C(13)−C(14) 1.555(7), C(14)−C(15)−C(16) 1.212(5), C(14)−C(15)−C(16) 1.212(5), C(14)−C(15)−C(16) 1.212(5).
of all 24 macrocyclic atoms from their least-squares plane is 0.442 Å. The distortion mode is quite different from that observed in, for example, the ruffled form of NiOEP\(^{D}\) where \(S_4\) ruffling is found. Here the distortion is asymmetric with regard to the two porphyrin faces. Larger displacements are observed for the \(C_m\) positions [1 Å for C(5) and C(15) versus 0.79 Å for C(10) and C(20)] bearing the tert-buty1 groups pointing away from the side with the axial ligand, and similarly a smaller pyrrole tilt is found for the pyrrole bent towards the axial ligand. This shows that the presence of the axial ligand hinders further out-of-plane distortion on the porphyrin face bearing the axial ligand. The degree of ruffling found in the present compound with \(C_m\) displacements of about 1 Å is so far unparalleled by any other porphyrin structure. The best known example for a ruffled porphyrin, Ni\(^{II}\) OEP, shows \(C_m\) displacements of 0.5 Å.\(^{e, f}\) The coordination geometry about the pentacoordinated zinc(t) centre with its out-of-plane displacement by 0.39 Å and an axial ligand Zn–N\(_1\) bond length of 2.165(4) Å agrees well with data found for other planar\(^g\) and nonplanar\(^a\) porphyrins. The Zn–N\(_1\) bond lengths are on average 2.014(5) Å, which is shorter than distances found in other Zn\(^{II}\) porphyrins. This is in accord with data found for example for Ni\(^{II}\)OEP with planar versus ruffled macrocycles.\(^{a, g}\)

In order to address the question whether the nonplanar conformation found in the solid state is retained in solution, we have compared the absorption spectra of some related porphyrins. Prior work has shown that a direct correlation exists between the degree of bathochromically shifted absorption bands and the extent of macrocycle distortion.\(^\text{1b}\) We chose 5,10,15,20-tetra(n-butyl)porphyrin (H\(_2\)TnBuP) as reference compound for a planar tetraalkylporphyrin. A comparison of this compound with H\(_2\)TiPrP and 5,10,15,20-tetra(isopropyl)porphyrin (H\(_2\)TiPrP), the Ni\(^{II}\) complex\(^x\) of which exhibits \(S_4\) ruffling of a lesser degree than found in H\(_2\)TiBuP, is given in Table 1. Both in the free base and zinc(t) series only small differences are found between the isopropyl and n-butyl derivatives, indicating a similar conformation, while in the dication series the isopropyl derivative shows somewhat more bathochromically shifted bands.\(^x\) The special case of H\(_2\)TiBuP is clearly evidenced by the significantly red-shifted absorption bands. Compared to the n-butyl derivatives the Soret band in the Zn\(^{II}\) derivative is shifted by 31 nm and the long wavelength band by 46 nm. Even more drastic are the differences in the dication series with a red shift of 72 nm for the long wavelength absorption band upon going from the n-butyl to the tert-buty1 derivative. These data clearly indicate that a very nonplanar macrocycle conformation is retained in solution. The present structural data and the unusual reactivity observed for H\(_2\)TiBuP make this and related derivatives very promising compounds for further mechanistic, structural and physicochemical investigations, which are currently in progress.

Support of this work from the National Institutes of Health (K. M. S., HL-22252) and the Deutsche Forschungsgemeinschaft (M. O. S.) is gratefully acknowledged.

Received, 7th November 1994; Com. 4/06785A

---

**Footnotes**

\(^a\) New address: Institut für Organische Chemie (WE02), Freie Universität, Takustrasse 3, D-14195 Berlin, Germany.

\(^b\) Crystal data for Zn\(^{II}\)TiBuP: small green plates were grown by slow diffusion of pyridine into a concentrated solution of Zn\(^{II}\)TiBuP in methylene chloride. C\(_{41}\)H\(_{49}\)N\(_5\)Zn M\(_\text{w}\) 677.2; triclinic, space group P\(_1\), \(a = 11.838(5), b = 12.229(4), c = 14.504(4)\) Å, \(\alpha = 102.96(2), \beta = 112.40(2), \gamma = 112.30(2)\)°; \(Z = 2, V = 1750.0(8)\) \(\text{Å}^3\); \(D_\text{c} = 1.285\) Mg m\(^{-3}\), \(\rho = 1.243\) A\(^{-1}\).

---

**References**


