Conformational Flexibility in Dodecasubstituted Porphyrins

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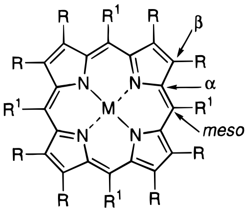
Interest in how nonplanar conformational distortions affect the properties of tetrapyrroles, in particular their biological function, has led to the synthesis of sterically crowded and highly nonplanar model systems such as **1**−**4**.[1] More than 30 crystal structures have now been reported for this group of dodecasubstituted porphyrins, sufficient to allow some conclusions to be drawn regarding the conformational preferences and flexibility of these novel macrocycles. Generally, the crystallographic data reveals a strong preference for a saddle conformation, with or without a small amount of ruffle distortion (see Figure 1). However, in contrast to regular porphyrins (e.g., NiOEP, of which there are three known crystalline forms exhibiting both planar and ruffled conformations),[2] dodecasubstituted porphyrins have not so far been demonstrated to possess a high degree of conformational flexibility. To determine if this is a general feature of dodecasubstituted porphyrins, we have undertaken an investigation of the conformational properties of the dodecaarylporphyrins **4**−**6**. We show herein that crystal structures of these porphyrins provide ample evidence of the significant conformational flexibility that can be observed for dodecasubstituted porphyrins; the structures we report include the first highly ruffled dodecasubstituted porphyrin, the first examples of multiple conformations in a single dodecasubstituted porphyrin, and the first "wave" core structure of a dodecasubstituted porphyrin, which is also the most nonplanar wave structure reported to date for any porphyrin.



	R	R¹
1	Et	C_6H_5
2	Et	NO_2
3	Br or Cl	Aryl
4	C_6H_5	C_6H_5
5	4-F-C_6H_4	C_6F_5
6	C_6H_5	C_6F_5

M = 2H or metal

Figure 2a−d shows the crystal structures of the nickel(II) complexes of porphyrins **4**−**6**. The crystal structure of **4** (M = Ni)[3,4a] (Figure 2a) demonstrates a well-defined ruffled core conformation, a deformation mode not previously observed in the sterically crowded dodecasubstituted porphyrin series. A maximum displacement of 0.855(7) Å (for C_{meso}) and an average displacement of 0.430(7) Å of the core atoms from the porphyrin mean plane (based on a least-squares plane calculated for the 24 core atoms) were observed, making this one of the most ruffled porphyrins ever reported. The pyrrole rings exhibit twist angles of 22.81(16)° (with respect to the porphyrin mean plane) and Ni−N distances of 1.909(5) Å. In contrast, the closely related porphyrin **5** (M = Ni)[4b] (Figure 2b) crystallizes in a well-defined saddle conformation; in this case, a maximum displacement of 1.014(3) Å (for C_β), and an average displacement of 0.542(4) Å for the core atoms from the porphyrin mean plane was observed. Pyrrole tilt angles (relative to the porphyrin mean plane) of 22.77(9)° and Ni−N distances of 1.911(5) Å were observed. Interestingly, for **6** (M = Ni, 1 and 2)[4c,d] two significantly different crystalline forms (Figure 2c,d) were apparent; these represent the first documented occurrence of this phenomenon in a dodecasubstituted porphyrin. The two crystalline forms were found to have different proportions of ruffle and saddle distortions with one form possessing a more ruffled conformation [**6** (M = Ni, 1)] and the other a more saddled conformation [**6** (M = Ni, 2)]. In **6** (M = Ni, 1), a maximum displacement of 0.859(4) Å (for C_{meso}), an average displacement of 0.482(4) Å for the core atoms from the porphyrin mean plane, and pyrrole twist angles of 30.98(10)° were observed. In **6** (M = Ni, 2), a maximum displacement of 0.926(5) Å (for a C_β), an average displacement of 0.461(5) Å for the core atoms from the porphyrin mean plane, and pyrrole tilt angles of 22.42(10)° were observed. The Ni−N distances for **6** (M = Ni, 1 and 2) were 1.892(3) and 1.916(3) Å, respectively. Thus, in contrast to other dodecasubstituted porphyrins, the nickel complexes of porphyrins **4**−**6** are capable of adopting a surprisingly wide range of core conformations.

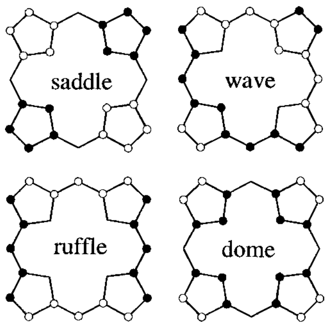


Figure 1. The four symmetrical nonplanar distortions commonly encountered for porphyrins which correspond with the lowest energy normal vibrational modes of the porphyrin macrocycle.[6] Filled circles correspond to atoms above the least-squares plane (calculated for the 24 atoms of the porphyrin core), and open circles represent atoms below the plane; atoms not circled are in the plane.

Figure 2e−g show the crystal structures of metal-free porphyrins **4**−**6**. The only previously published structure of a

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(1) Ravikanth, M.; Chandrashekar, T. K. *Struct. Bonding (Berlin)* **1995**, *82*, 105.

(2) Brennan, T. D.; Scheidt, W. R.; Shelnutt, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 3919.

(3) Complete details of the syntheses and spectroscopic characterization of porphyrins **4**−**6** will be presented elsewhere: Van Caemelbeck, E.; Forsyth, T. P.; Kadish, K. M.; Ma, J.; Medforth, C. J.; Nurco, D. J.; Shelnutt, J. A.; Showalter, M.; Simpson, M. C.; Smith, K. M.; Song, X.; D'Souza, F.; Taylor, K. K. Manuscript in preparation.

(4) (a) **4** (M = Ni)·5.8(C_6H_{12})·0.9($CHCl_3$). A red prism crystallized in the cubic space group *F*4 3*c*. Cell dimensions were $a = b = c = 40.950(5)$ Å, $V = 68669(14)$ Å^3, and $Z = 24$. Final *R* factors were $R_1 = 0.089$ (observed data) and w$R_2 = 0.288$ (all data); the GOF (based on F^2) was 1.026. (b) **5** (M = Ni)·5(C_6H_{12}). A red block crystallized in the tetragonal space group *P*4$_2$/*nmc*. Cell dimensions were $a = 24.394(2)$ Å, $c = 8.6590(11)$ Å, $V = 5152.7(10)$ Å^3, and $Z = 2$. Final *R* factors were $R_1 = 0.054$ (observed data) and w$R_2 = 0.156$ (all data); the GOF (based on F^2) was 0.914. (c) and (d) **6** (M = Ni), full details will be reported elsewhere: Nurco, D. J.; Fajer, J.; Smith, K. M. Manuscript in preparation. (e) Medforth, C. J.; Senge, M. O.; Smith, K. M.; Sparks, L. D.; Shelnutt, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 9859. (f) **5** (M = 2H). A purple needle crystallized in the monoclinic space group *P*2$_1$/*c*. Cell dimensions were $a = 16.6290(10)$ Å, $b = 8.7210(10)$ Å, $c = 25.700(3)$ Å, $\beta = 105.590(10)$°, $V = 3589.9(6)$ Å^3, and $Z = 2$. Final *R* factors were $R_1 = 0.055$ (observed data) and w$R_2 = 0.109$ (all data); the GOF (based on F^2) was 1.063. (g) **6** (M = 2H)·4(CH_2Cl_2). A purple needle crystallized in the tetragonal space group *I*4$_1$/*a*. Cell dimensions were $a = 28.605(2)$ Å, $c = 9.9690(10)$ Å, $V = 8157.1(11)$ Å^3, and $Z = 4$. Final *R* factors were $R_1 = 0.040$ (observed data) and w$R_2 = 0.117$ (all data); the GOF (based on F^2) was 0.727.

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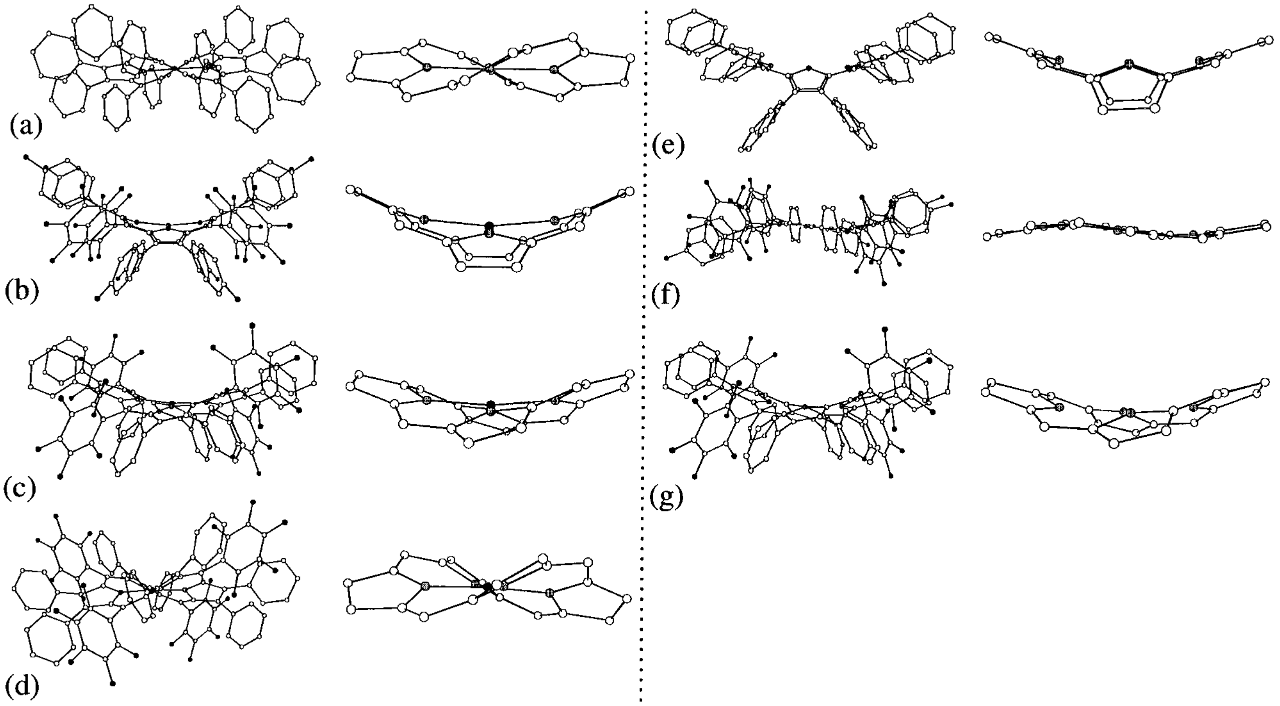

Figure 2. Crystal structures of dodecaarylporphyrins with expansions of the porphyrin cores. Left panel: (a) **4** (M = Ni); (b) **5** (M = Ni); (c) **6** (M = Ni, 2); (d) **6** (M = Ni, 1). Right panel: (e) **4** (M = 2H); (f) **5** (M = 2H); (g) **6** (M = 2H).

dodecaarylporphyrin is that of **4** (M = 2H)[4e] (Figure 2e). This porphyrin crystallized in a saddle conformation as opposed to the ruffled structure seen for the corresponding nickel(II) complex (Figure 2a). The structure is similar to **5** (M = Ni) except that the pyrrole rings are alternately tilted out of plane by differing degrees (18.0° and 33.6°, respectively). A maximum displacement of 1.160 Å (for a C_β) and an average displacement of 0.485 Å for the core atoms, from the porphyrin mean plane, were reported. The crystal structure determined for **5** (M = 2H)[4f] (Figure 2f) is dramatically different from that of the corresponding nickel(II) complex and from the structure of **4** (M = 2H). In **5** (M = 2H), the macrocycle shows an unusually pronounced "wave" conformation which has not previously been observed for dodecasubstituted porphyrins and which has been reported only infrequently in the porphyrin literature.[5,6] In this structure, one pair of opposing pyrrole rings are tilted up and down by 9.1(2)°, while the other opposing pair of pyrrole rings are twisted by 7.5(2)° with respect to the porphyrin mean plane. Additionally, a maximum displacement of 0.244(4) Å (for a C_β) and an average displacement of 0.116(4) Å for the core atoms from the porphyrin mean plane were observed. Although the core displacements for **5** (M = 2H) are small when compared with the other structures reported herein, they are considerably larger than those seen for the most nonplanar wave structure in the literature (7,8,17,18-tetrabromo-5,10,15,20-tetramesitylporphyrin),[5] which exhibits a maximum displacement of 0.129 Å and an average displacement of 0.065 Å for the core atoms from the porphyrin mean plane]. A second crystalline form of **5** (M = 2H), for which the crystal structure could not be reliably determined, was also obtained; this possessed cell dimensions similar to those seen for **5** (M = Ni) and **5** (M = Co^{II}) (structure not shown), suggesting that this porphyrin can also crystallize with a saddle-type core conformation. Finally, the crystal structure of **6** (M = 2H)[4g] (Figure 2g) shows a combination of saddle and ruffle distortions, much like those observed in (**6** M = Ni, 2). A maximum displacement of 0.838(4) Å (for a C_β), an average displacement of 0.400(4) Å for the core atoms from the porphyrin mean plane, and pyrrole twist angles of 21.13(9)° were observed.

The structures reported herein for nickel(II) complexes and metal-free porphyrins **4**−**6** clearly indicate that these porphyrins possess a higher degree of conformational flexibility than has previously been observed for other dodecasubstituted porphyrins. Interestingly, this increased conformational flexibility is also apparent in molecular mechanics calculations of **4** (M = Ni), which revealed a range of structures with similar energies but different amounts of ruffle and saddle distortion.[4e] This observation further validates the use of molecular techniques for the design of porphyrins with specific conformational properties and/or 3-D structures. We are now investigating whether spectroscopic techniques (e.g., resonance Raman spectroscopy) can be used to detect the presence of multiple nonplanar conformations of the dodecaarylporphyrins in solution,[3] with the ultimate aim of differentiating nonplanar conformations of tetrapyrroles in biological systems.[1]

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Supporting Information Available: Tables of crystallographic experimental details, atomic coordinates and isotropic displacement parameters, bond lengths, bond angles, anisotropic displacement parameters, hydrogen coordinates, and thermal ellipsoid plots for compounds **4** (M = Ni), **5** (M = 2H, Ni), and **6** (M = 2H) (49 pages). See any current masthead page for ordering and Internet access instructions.

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