Structure and Conformation of Tetra-*meso*-, Octa-β-, and Dodecasubstituted 22,24-Dihydroporphyrins (Porphyrin Dications)

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A comparative crystallographic analysis of the conformation of porphyrin diacids with various substituent types reveals considerable differences in the degree of nonplanarity and distortion modes. Diacids of 5,10,15,20-tetraarylporphyrins generally exhibit typical saddle-distorted macrocycles with displacements of the C_b positions in the range of 0.7–1.0 Å. Adding peripheral substituents, *i.e.*, using dodecasubstituted porphyrins for the diacid formation yields similar distortion types albeit with larger out-of-plane displacements. As a result of the combined effect of both peripheral (interaction between the C_b and C_m substituents) and core (interaction between the four inner hydrogen atoms) steric strain the maximum C_b displacements reach 1.3–1.5 Å. Quite a different situation is observed for the diacids of 2,3,7,8,12,13,17,18-octaalkylporphyrins. Here, macrocycles with pair-wise displacement of neighboring pyrrole rings and significant NH pyramidalization and those with classic saddle distortion are found. Generally, octa-β-substituted porphyrin diacids show smaller degrees of nonplanarity; C_b displacements ranged from 0.06 to 0.72 Å. On the basis of the overall degree of conformational distortion (Δ24 = average deviation of the 24 macrocycles atoms from the mean plane), the three different types of porphyrin macrocycles studied differ considerably in their degree of conformational flexibility. For several porphyrin crystal structures with different counterions and/or solvate molecules were obtained. Taking into account results from the literature 2,3,7,8,12,13,17,18-octaethyl-22,24-dihydro-5,10,15,20-tetraphenylporphyrin (**13**) shows the smallest degree of flexibility (Δ24 = 0.61–0.63 Å; four different X-ray structures), while 22,24-dihydro-5,10,15,20-tetraphenylporphyrin (**1**) is more flexible (Δ24 = 0.42–0.52 Å; four structures). The largest flexibility is observed for 2,3,7,8,12,13,18-octaethyl-22,24-dihydroporphyrin (**7**) (Δ24 = 0.02–0.33 Å; four structures).