A Conformational Study of 5,10,15,20-Tetraalkyl-22\(H^+\),24\(H^+\)-porphyrindiium Salts (Dication Salts)

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N-protonation of 5,10,15,20-tetraalkylporphyrins with \(n\)-butyl, isobutyl, isopropyl, 1-ethylpropyl or tert-butyl substituents yields the respective 22,24-dihydroporphyrins (22\(H^+\),24\(H^+\)-porphyrindiium salts) that exhibit highly nonplanar conformations. Depending on the steric demand of the meso substituents, the free base porphyrins have planar to moderately ruffled macrocycles (primary or secondary alkyl residues) or are severely ruffled (tertiary alkyl residues). X-ray crystallographic studies show that protonation of porphyrins with \(n\)-Bu (2), i-Pr (3) or EtPr (4) substituents leads to steric congestion of the core resulting in symmetric, saddle distorted macrocycles as evidenced by average displacements of the \(C_b\) positions from the mean plane ranging from 0.79 to 1.01 Å. The structures observed for these porphyrin diacids are very similar in distortion mode and degree of nonplanarity to 5,10,15,20-tetraaryl-22\(H^+\),24\(H^+\)-porphyrindiium salts and to 2,3,7,8,12,13,17,18-octaalkyl-5,10,15,20-tetraarylporphyrins. In contrast, protonation of the highly ruffled 5,10,15,20-tetrakis(tert-butyl)porphyrin results in a switch of the conformational distortion mode. The dication 6 shows both saddle distortion (\(C_b\) displacements ~1.3 Å) and ruffling of the macrocycle (\(C_m\) displacements of approx. 0.48 Å). Thus, the need to accomodate four N-H units in the porphyrin core with its associated out-of-plane tilting of the pyrrole rings and the steric strain induced at the meso carbon atoms results in a highly nonplanar porphyrin with mixed distortion modes.