



Review

Sterically induced distortions of nickel(II) porphyrins – Comprehensive investigation by DFT calculations and resonance Raman spectroscopy



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ABSTRACT

A series of 5,15-disubstituted and 5,10,15,20-tetrasubstituted, and 5,10,15,20-tetrasubstituted-2,3,7,8,12,13,17,18-octaethyl nickel(II) porphyrins in dichloromethane is reported to comprehensively access their sterically induced distortions from planarity. Thus, the tutorial review focuses on both resonance Raman spectroscopic investigations and structural investigations based on DFT. We relate different theoretical and experimental methodologies to predict out-of-plane distortions of the porphyrin macrocycles which are quantified by normal-coordinate structural decomposition. This comprehensive compilation reveals shortcomings in the molecular mechanic calculations and illustrates the impact of crystal packing forces on crystal structures. Non-planar distortions shift the experimentally observed resonance Raman marker bands ν_2 , ν_3 and ν_4 to lower frequency. A revised correlation between this shift and the calculated structural parameter (ruffling angle) is presented and reveals deviations from reported correlations based on molecular mechanics.

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1. Introduction

Metalloporphyrins are an unique class of compounds with a wide variety of applications. They are utilized for light harvesting in, e.g., dye-sensitized solar cells [1] reaching efficiencies of up to 13% [2] and thus, exceeding the efficiency obtained with ruthenium-complex based devices while avoiding the cost incurred using the expensive metal ruthenium [3]. Besides their light harvesting properties metalloporphyrins also attract attention due to their electrocatalytic activity [4]. Hydrogen and oxygen evolution reactions catalyzed by nickel porphyrins have been reported [5,6] as well as nickel porphyrin-based electrochemical sensors to detect nitric oxide release from a single cell [7,8]. Furthermore, the unique diagnostic and therapeutic potential of porphyrins, e.g., in tumor detection, tumor imaging and in the photodynamic treatment of malignancies are important motivations for porphyrin research [9–11]. Porphyrins are a ubiquitous class of compounds in nature. Classic examples are hemes, a group of iron porphyrins which serve as cofactor in proteins with multiple biological functions. Proteins such as myoglobin and hemoglobin are involved in reversible oxygen binding, while cytochromes function in reversible electron transfer processes. On the other hand, cytochromes P450 and peroxidases can perform oxidative transformations with a wide range of substrates [12]. The versatile biochemistry of cytochromes P450 has triggered the industrial applications of P450s for the production of fine chemicals [13,14]. P450s allow for a variety of regio- and enantioselective oxidation reactions, which are difficult to achieve by chemical synthesis [13,14].

The wide-range use of porphyrins is related to the unique properties of the porphyrins macrocycle: The large delocalized π -system leads to pronounced absorption in the visible range [15] and stabilizes various oxidation states of the central metal ions [16]. Additionally, the structural flexibility of the porphyrin macrocycle is remarkable and significantly impacts the optical, chemical and electronic properties of porphyrins [17,18]. Coordination of metal ions, which are small compared to the cavity size of the planar porphyrin, induces out-of-plane (*oop*) distortions [17,19,20], for example, nickel(II) ions. The optimal metal–nitrogen distance for a planar metalloporphyrin is about 2.01 Å [21,22], while Ni–N bonds prefer a shorter bond length of 1.85 Å [23]. As a result, the Ni–N bonds pull the pyrrole rings toward the center which induces *oop* deformations of the macrocycle. The actual degree of non-planarity is determined by the energetic trade-off between the energy gain from shorter Ni–N bonds within the contracted core of a non-planar porphyrin and the energy penalty arising from a decreased conjugation within the π -system of a non-planar porphyrin. The presence of substituents on the periphery of the macrocycle induces steric strain, which additionally contributes to non-planar distortions of nickel porphyrins. Thus, nickel porphyrins have been used to study the effect of non-planar distortions on the properties of porphyrins and to mimic conformationally distorted porphyrins found *in vivo* [18,24,25].

Distortion of the porphyrin macrocycle, in particular also the *oop* distortions of the macrocycle, have a significant impact on the chemical and photo-physical properties of nickel porphyrins [18], e.g., its affinity to axial ligation [26,27], redox potentials [28,29], optical absorption [30,31] and excited state relaxation processes [25,32,33]. It can be demonstrated that the photo-physical properties of nickel porphyrins can be gradually altered by increasing the degree of non-planarity of the heterocycle, i.e., by gradually increasing the steric demand of peripheral substituents [25,26,28]. This highlights the possibility to fine-tune the photo-physical parameters of nickel porphyrins for a given application by controlling the degree and type of *oop* distortion.

In order to understand the impact of *oop* distortions on the physical and chemical properties of metalloporphyrins, the type and degree of *oop* distortions have to be defined: Shelnutt and co-workers [34,35] introduced the concept of normal-coordinate structural decomposition (NSD), which represents a given macrocycle structure by displacements along the normal coordinates of a D_{4h} -symmetric reference macrocycle (see Fig. 1 and for details Chapter 2). In most cases [34], the observed non-planarity can be

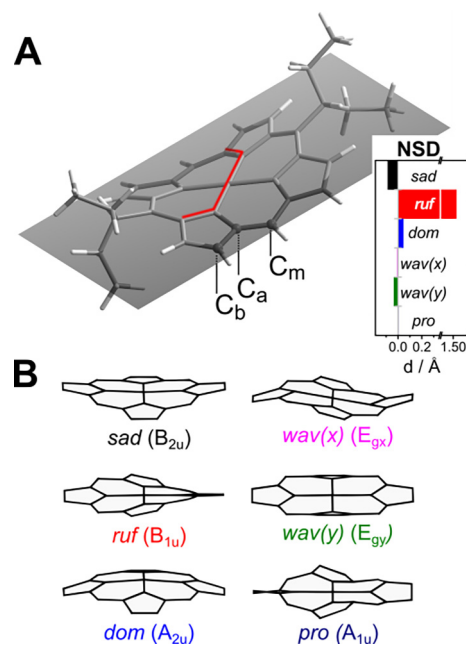


Fig. 1. Structure of **NiD(1-Et-Pr)P** – calculated at the DFT level of theory – reveals the out-of-plane distortion of the porphyrin macrocycle (A). Displacements d (in Å) along the lowest-frequency out-of-plane normal coordinates are determined by normal-coordinate structural decomposition (NSD, results in bar chart). The effect of a 1 Å deformation is illustrated for each of these normal-coordinates (B, adopted from Ref. [66]). Figure A highlights one of the ruffling dihedral angles $\text{cis-C}_\alpha\text{-N-N-C}_\alpha$ (red line), the mean-square plane – determined by the 24 macrocycle atoms – (grey plane) and the position of meso (C_m), α (C_α) and β (C_β) carbon atoms.

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