

## Fixation of Neutral Molecules in the Binding Cavity of Nonplanar Porphyrins – A Third Dodecaphenylporphyrin Modification with NH-Solvent Hydrogen Bonding

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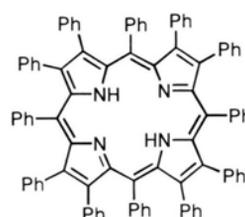
Porphyrins, Steric Strain, Conformational Flexibility, Crystal Structure, Hydrogen Bonding

A third crystalline modification of dodecaphenylporphyrin is described in which the pyrrole nitrogen atoms are hydrogen-bonded to two ethanol molecules. This is the first crystallographic proof for the accessibility of nitrogen atoms in saddle-distorted free base porphyrins for hydrogen bonding. No such coordination is possible in either planar or ruffled porphyrins. Thus, the possibility exists to utilize conformationally distorted porphyrins for the binding of neutral molecules.

Highly substituted porphyrins often are severely distorted macrocycles [1]. Depending on the type, location and number of substituents, specific conformations can be realized. For example, dodeca-substituted porphyrins with *meso* aryl groups exhibit saddle-distorted macrocycles (large out-of-plane distortions of the  $\beta$  pyrrole positions  $C_\beta$ ) [2,3], while porphyrins with *meso* alkyl groups often show ruffled conformations (large out-of-plane distortions of the *meso* positions  $C_m$ ) [4–6]. In recent years several cases of multiple crystalline modifications of dodecasubstituted porphyrins have been described and used as examples for the inherent conformational flexibility of the tetrapyrrole macrocycle system. Notably, dodecaarylporphyrins appear to be prone to crystallize in different conformations ranging from highly nonplanar to planar despite the high degree of peripheral substitution [7,8]. As conformational distortion results in macrocycles with significantly altered physicochemical properties that have biological relevance, the investigation of the con-

formational flexibility of highly substituted porphyrins is of continuing interest [1].

Early on it was realized that one of the inherent properties of nonplanar porphyrins is their ability to bind small molecules in the cavities formed by the nonplanar macrocycle [1]. Almost all crystal structures of such systems show the inclusion of solvent molecules in these binding pockets. Recently it was suggested that hydrogen bonding of solvate molecules to the pyrrole nitrogen atoms in highly substituted free base porphyrins might be a further way to modulate the electronic absorption properties of such systems [9]. In this context we report here on a third crystalline modification of dodecaphenylporphyrin that for the first time gives a structural example of a porphyrin that has two ethanol of solvation bonded directly to the core.



H<sub>2</sub>DPP

Two orthorhombic conformations of H<sub>2</sub>DPP have been described in the literature [4,8]. The first (space group  $Cmc2_1$ ), crystallized with three methylene chloride molecules of solvation [4]. The other crystallized in space group  $Pnma$  with three water molecules of solvation [8]. Both modifications showed inclusion of solvate molecules in the crystal lattice, however, without any direct coordination to the porphyrin core. Their overall conformation can be described as a saddle. Nevertheless, distinct differences in the individual conformations were observed. The  $Pnma$  modification (orthorhombic B) showed a symmetric saddle distortion with similar out-of-plane displacements for individual pyrrole rings (average  $C_\beta$  displacements of 1.32 Å). Opposed to this, the  $Cmc2_1$  modification (orthorhombic A) exhibited an asymmetric saddle distortion with larger  $C_\beta$  displacements for every second pyrrole ring (1.28 Å versus 0.71 Å) (Table I). The asymmetric distortion is clearly evidenced in the skeletal deviation plots given in Fig. 1.

