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Substitution Architecture Control of the Macrocycle Nonplanarity in the Free Base Corroles

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It is well known, that the planar porphyrin macrocycle undergoes the transformation into the highly distorted nonplanar molecule upon the increasing loading with peripheral substituents is well known [1]. In case of the corroles the situation is more complicated upon increase in the crowding at the periphery of macrocycle since the corrole macrocycle is inherently nonplanar and it is able to adopt either the molecular conformation with the higher degree of nonplanar distortions of the same type or to undergo the conformational switch to the another type of macrocycle distortion when sufficient amount of the sterical strain accumulates at the macrocycle periphery.

The basis of the nonplanar distortions analysis is the deviation calculations of macrocycle atoms from the macrocycle mean plane. In the case of porphyrins the mean plane is selected as a plane with a minimum sum of mean square deviations of all the 24 macrocycle atoms. Almost all the macrocyclic atoms of the unsubstituted porphin molecule, tetraphenylporphyrin molecule or octaalkyl-substituted derivatives are in the mean plane. In case of corroles the selection of the macrocycle mean plane is difficult because of the asymmetry of the molecule: not all the macrocycle atoms are equivalent. In addition, the macrocycle mean plane must be the same for the two NH tautomers, i.e. it must remain invariant under NH tautomerization so that the analysis of geometric parameters of the molecule was carried out in the same basis. As a macrocycle mean plane we have proposed earlier the plane defined as one with minimal mean square deviations of C1, C4, C5, C6, C9, C16 and C19 carbon atoms (hereinafter – the 7C plane), according to IUPAC nomenclature [2].

Aiming to see how the corrole macrocycle conformation depends on the architecture of peripheral substitution the theoretical study has been carried out. Molecular conformation of the tetrapyrrolic macrocycle for the family of alkylated derivatives of the free base corroles has been calculated by quantum-chemical methods. The methyl groups have been chosen as substituents to impose the maximum steric constrains for the macrocycle neighborhood due to the sp^3 -hybridization of carbon atom. A number of the attached alkyl substituents and their positioning at the periphery of macrocycle determine the character and degree of the nonplanar macrocycle distortions. The degree of the nonplanar macrocycle distortions was treated as the $\Delta 23$ parameter, which is the average least-square deviation from the mean macrocycle plane C7 per one macrocycle atom [2]. The analysis of the obtained results will be presented in detail.

REFERENCES

1. Senge MO. *Chem. Commun.* 2006; 243–256.
2. Beenken WJD, Presselt M, Ngo TH, Dehaen W, Maes W and Kruk MM. *J. Phys. Chem. A.* 2014; **118**: 862-871.