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MACROCYCLE STRUCTURE IN PERIPHERICALY CROWDED FREE BASE CORROLES

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Corroles is known to be the specific family of tetrapyrrolic compounds with contracted macrocycles due to direct C_a-C_a linkage between two adjacent pyrrole rings. Macrocycle contraction leads to the bond alternation changes which, in turn, lead to the formation of the free base with three pyrrole and one pyrrolenene rings. Third proton brings additional sterical hindrance in the macrocycle core. As a result, the pyrrole rings tend to adopt alternate up and down positions relative to the core plane. Due to these factors the macrocycle of free base corroles reveals the pronounced nonplanar distortions.

The molecular conformation of the corrole macrocycle depends also on the type of peripheral substituents and the macrocycle substitution architecture. Introducing the numerous and bulky groups at the macrocycle periphery brings additional driving force for the macrocycle distortions. It is of interest to establish the interplay between these two opposed sterical constraints and elucidate the molecular conformations of such peripherically crowded corroles. In this work we are analyzing the molecular conformation of undecasubstituted 5,10,15-tris-penta-fluorophenyl-2,3,7,8,12,13,17,18-octa-bromo-corrole (A_3C_8-corrole) and to identifying its structural features in comparison with trisubstituted 5,10-dimesityl-15-2,6-dichloropyrimidinyl-corrole (AB_2-corrole) and tetrasubstituted 5,10,15-tris-phenyl-18-nitrocorrole (A_3C_1-corrole). The detailed structural analysis was carried out for the long-wavelength NH tautomers T1 of the above compounds. The geometry of molecules was calculated by quantum chemical methods (AB_2-corrole, A_3C_8-corrole) and/or obtained from X-ray diffraction data (A_3C_8-corrole, A_3C_1-corrole).

In the tetrasubstituted A_3C_1-corrole the three pyrrole rings (*A*, *C* and *D*, counted clockwise) are tilted to one direction, and that of ring *B* - to the other. In this case, the nitrogen atoms of the rings *A* and *D* are on the same side of the mean plane of the macrocycle, and the nitrogen atoms of the pyrrole rings *B* and *C* are on the other. Such a pattern is characteristic of an asymmetric wave-type distorted conformer [1]. The direction of wave-like distortion passes through the pyrrole rings *B* and *D*. For the trisubstituted AB_2-corrole the tilting pattern has the same features.

The deviations from the mean macrocycle plane for undecasubstituted A_3C_8-corrole differs significantly from the previous two cases. The diametral pairs of pyrrole rings (*A*, *C*) and (*B*, *D*) are inclined in opposite directions relative to the mean plane. The nitrogen atoms of the pyrrole rings in these pairs are located on different sides of the mean plane at various distances from it. Such a pattern should be attributed to a conformer with an asymmetric saddle-like type of macrocycle distortion. Asymmetry reveals itself in different angles of the pyrrole rings tilt. Thus, the introduction of bulk bromine atoms into 2,3,7,8,12,13,17 and 18

positions of pyrrole rings in the presence of three pentafluorophenyl groups leads to a strong steric interaction between Br atoms and *ortho*-fluorines, which leads to the formation of saddle-type conformer.

Nonplanar distortions degree for the corrole macrocycle has been determined with the Δ23 parameter, which is the average least-square deviation from the mean macrocycle plane per one macrocycle atom. The wave-like AB_2 and A_3C_1 corroles have similar values of parameter Δ23 equal to 0.200 and 0.215 Å, respectively. The undecasubstitution induces substantial increase in the amplitude of atom deviation from the mean plane. The value of the parameter Δ23 increases more than twice and is 0.503 Å for saddle-like A_3C_8-corrole. Thus, macrocycles of the free base corroles, in which the only reason for the formation of a nonplanar conformer is the steric interactions of three protons in the macrocycle core, are characterized by a moderate value of the Δ23 parameter and demonstrate the wave-like type of nonplanar distortion. Additional steric interactions at the periphery of the fully substituted macrocycle (i.e., undecasubstituted) of the free base corroles lead to a change in the type of nonplanar distortions to the saddling, which is characterized by a significantly larger value of Δ23. Upon transition from the wave- to saddle-like conformer, the dihedral angles characterizing the pyramidalization of the nitrogen atoms of the pyrrole rings remain practically unchanged. One can suggest that these values are characteristic for any conformation of the macrocycle of the free base corroles. Data for the geometry optimization of model compounds, where the magnitude of steric interactions was modulated via the substitution of multiple methyl groups, support this suggestion.

In summary, the analysis of the structure of tetrapyrrolic macrocycle of free base corroles, which differ in the peripheral substitution type, has been carried out. It has been found that tri- and tetrasubstituted corrole derivatives reveal the wave-type nonplanar distortions, whereas undecasubstituted (in the *meso*-positions and all the pyrrole rings) derivative has saddle-type distorted macrocycle. The degree of nonplanar distortions of corroles macrocycle has been determined with the Δ23 parameter, which is the average least-square deviation from the mean macrocycle plane C7 per one macrocycle atom. While the tri- and tetrasubstituted corrole derivatives with aryl substituents in the *meso*-positions reveal similar moderate Δ23 values, the undecasubstitution induces substantial increase in the amplitude of atoms deviation from the mean plane. Strong steric interaction between peripheral substituents leads to the pyrrole rings *A*, *B* and *C* are substantially tilted relative to the mean macrocycle plane 7C. These differences indicate that tetrapyrrolic macrocycle of the free base corroles has wave-like conformation in the absence of steric interactions with peripheral substituents, which holds upon weak steric interactions. When the eight bulky substituents introduced the conformational transition from the wave- to saddle-type distorted conformer takes place as a result of the enhancement of steric interactions in the peripherically crowded derivatives.

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