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MACROCYCLE NONPLANAR DISTORTIONS IN THE FREE BASE CORROLES

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The molecular conformation of the corrole macrocycle depends on the type of peripheral substituents and the macrocycle substitution architecture. The purpose of this work is to elucidate 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 identify 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 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 [1], A_3C_8-corrole [2]) and/or obtained from X-ray diffraction data (A_3C_8-corrole [8], A_3C_1-corrole [3]).

The diagrams of deviations Δz of macrocycle atoms of the A_3C_1- and A_3C_8-corroles from the mean plane of the macrocycle, taken as 7C plane [1], are shown on Fig. 1. The pyrrole (pyrrolenine) rings *A*, *B*, *C*, *D* are shown from left to right in the figure, and light circles denote nitrogen atoms.

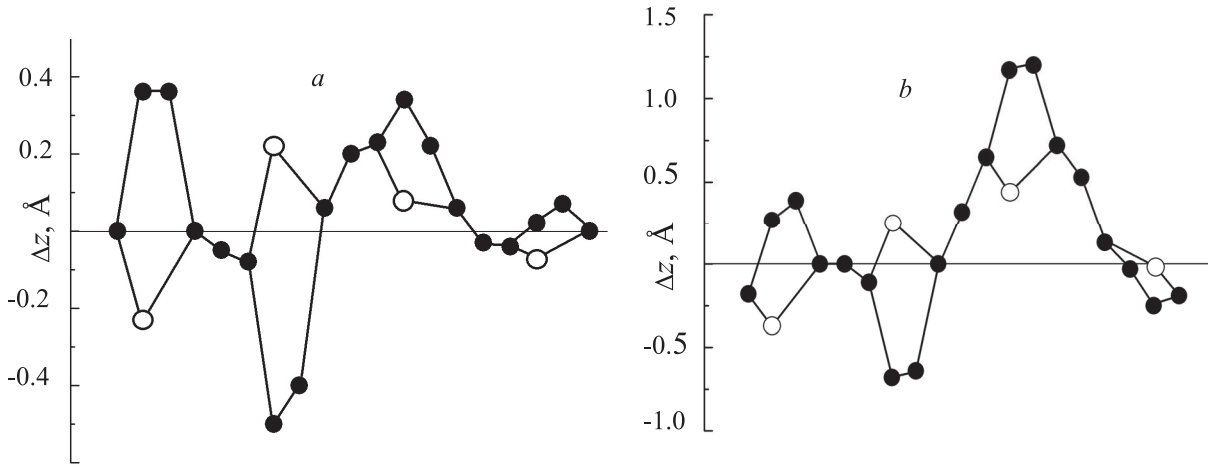

Fig. 1. *Diagram of deviations of the atoms from the mean plane of the macrocycle: a – A_3C_1 corrole; b – A_3C_8 corrole*

In the tetrasubstituted A_3C_1-corrole the pyrrole rings *A*, *C* and *D* 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. The direction of wave-like distortion passes through the pyrrole rings *B* and *D*. For the trisubstituted AB_2-corrole the diagram 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 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.

The degree of nonplanar distortions of 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 theperiphery 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 23. 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.

This work is a part of project supported by the Foundation for Fundamental Research of the Republic of Belarus, grant X16P-097.

References

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