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RELATIONSHIP BETWEEN THE CORROLE MACROCYCLE PERIPHERAL SUBSTITUTION TYPE AND CHARACTER OF ITS NONPLANAR DISTORTIONS

The analysis of the character of tetrapyrrolic macrocycle nonplanar distortions of free base corroles has been carried out. The molecular conformations of the corrole NH tautomers have been obtained with the quantum-chemical calculations (5,10-mesityl-15-2,6-dichloropyrimidinyl-corrole) and X-ray analysis (5,10,15-phenyl-18-nitro-corrole). The character of nonplanar distortions was found to be similar for corresponding NH tautomers of both corroles, this point out to the features of the NH tautomer molecular conformations. Despite the fact, that all three studied molecular conformations have wave-type nonplanar distortions, the magnitudes of deviations for individual atoms are noticeably different. To estimate quantitatively the nonplanar macrocycle distortions of the corrole macrocycle the $\Delta 23$ value has been introduced for the first time. $\Delta 23$ value is the average least-square deviation from the mean macrocycle plane $C7$ per one macrocycle atom. Small increase in the $\Delta 23$ value has been found for the 5,10,15-phenyl-18-nitro-corrole. It is likely to be due to synergism of the macrocycle nonplanar deformation and rotation of aryl substituents in the meso-positions. It was shown that asymmetry of corrole molecular conformation is similar to that of sterically hindered porphyrins having the bulky substituents grouped on the one moiety of macrocycle. However, in case of corroles sterical hindrance is in the macrocycle core, leading to the wave-type macrocycle, whereas in case of porphyrins the sterical factors are on the macrocycle periphery, resulting in the saddle-type distorted conformer.

Key words: corrole, NH tautomer, porphyrin, macrocycle mean plane, nonplanar distortions.

Introduction. The molecular conformation of the corrole free bases and their metal complexes is the subject of discussion. It is known that there is no of one of the carbon atoms in the *meso*-position of the corrole macrocycle, whereby two of the pyrrole fragments are bound directly by a C_a-C_a bond. As a result, corroles form a contracted macrocycle, in which the size of core is smaller compared to those in porphyrins. The distance between the protons attached to nitrogen atoms at the opposite pyrrole rings, is close to the sum of their van der Waals radii, resulting in the flatness distortion of macrocycle. Moreover, the decrease of the size of π -conjugated macrocyclic contour leads to a change in the character of bond alternation. As a result the free base corrole molecule contains three protons in its core (three pyrrole and one pyrroline rings), rather than two, compared to the free porphyrin base molecules (two pyrrole and two pyrroline rings). Increase in the number of protons in the nucleus of the macrocycle, as stated earlier for the protonated porphyrin forms [1], also leads to distortion of the planar structure of the corrole macrocycle. However, reducing the distance between a pair of adjacent pyrrole and pyrroline rings brings the conditions for the formation of an intramolecular hydrogen bond, which is a contributing factor to the planarization of the tetrapyrrolic macrocycle. Thus, the molecular conformation of the corrole macrocycle is defined as the result of simultaneous action of several factors. Contribution factors can vary both under the influence of external conditions (physico-chemical properties of the molecule microenvironment) and

depending on the structure (peripheral macrocycle substitution type) of the corrole molecule. Analysis of the role of the latter one is complicated by the fact that corrole molecules have reduced symmetry: point symmetry group is not higher than C_s , while the free bases porphyrin belong to point symmetry group D_{2h} . Decrease in the molecular symmetry for the free base corroles allows the possibility of their existence in the form of two tautomers, with different electron structure and macrocycle conformation as a result of various protons location in the macrocycle core. We have shown [2–6] that NH tautomers are actually observed for the free base corroles with different types of peripheral substitution (AB_2 -, A_2B - и A_3 -corroles), even in liquid solutions at room temperature.

The purpose of this paper is to analyze the nature of the nonplanar tetrapyrrolic macrocycle distortions of the corrole free bases for molecular conformations derived from quantum chemical calculations [5], X-ray structural analysis [7] and to compare their characteristics with the nonplanar distortions identified in the free bases porphyrins. As objects of study chosen 5,10-mesityl-15-2,6-dichloropyrimidinyl-corrole (hereinafter – AB_2 -corrole) and 5,10,15-phenyl-18-nitro-corrole (hereinafter – A_3 -corrole) have been chosen as subjects of research. Molecular conformations of the two NH tautomers (T1 and T2) for AB_2 -corrole have been calculated by quantum-chemical methods, while the molecular structure of T1 tautomer for the A_3 -corrole has been identified by X-ray structural analysis.

Main part. The basis of the nonplanar distortions analysis is the deviation calculations of

macrocycle atoms from the macrocycle mean plane [8]. 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 porphyrin 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 a plane defined as one with minimal mean square deviations of C1, C4, C6, C9, C16 and C19 atoms (hereinafter – the 7C plane) [5, 6]. The structure of the NH corrole tautomers with the numbering of the macrocycle atoms according to IUPAC nomenclature is shown in Fig. 1, where the black circles indicate atoms whose coordinates are used to calculate the average mean plane of the macrocycle. Previously we have reported that both NH tautomers are characterized by nonplanar *wave-like* distortions, but the amplitude of the deviations of individual atoms of the macrocycle varied noticeably [6].

However, the amplitude deviations of the individual atoms of the mean plane of the macrocycle did not allow quantifying the magnitude of non-planar macrocycle distortions as a whole. The parameter Δ_{24} has been introduced when analyzing non-planar distortions of the porphyrin tetrapyrrolic macrocycle. The parameter is a mean deviation calculated for 24 macrocycle atoms [8]. To characterize the non-planar distortions of the reduced corrole macrocycle containing 23 atoms, we have introduced the Δ_{23} value:

$$\Delta_{23} = \sqrt{\frac{1}{23} \sum_{i=1}^{23} \Delta z_i^2},$$

where Δz_i is deviation an i -th atom of macrocycle from the macrocycle mean plane (7C plane). Analysis of the calculated Δ_{23} values shows that both AB₂-corrole NH tautomers exhibit identical (within error) nonplanar distortions (0.200 and 0.198 Å for T1 and T2 tautomers respectively). At the same time, for A₃-corrole there is a slight increase of the value $\Delta_{23} = 0.215$ Å. The comparison of values for two corroles has shown that the observed trend in the Δ_{23} value can be explained by the difference in the rotational degree of freedom of aryl substituents in the macrocycle *meso*-positions.

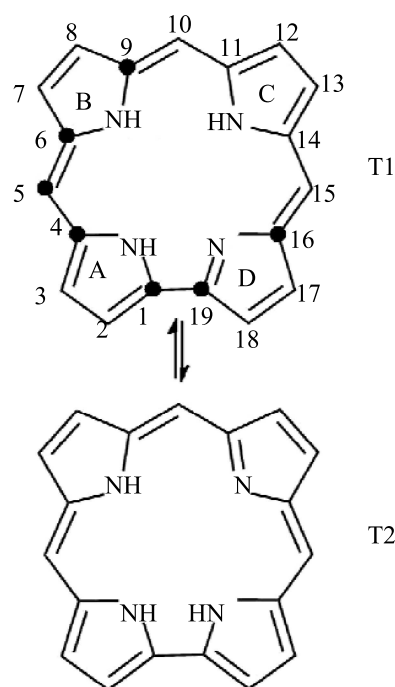


Fig. 1. NH tautomer structure of the free base corrole. Figures indicate the macrocyclic atoms numbering according to the IUPAC nomenclature. Black circles represent carbon atoms, the coordinates of which are used to calculate the macrocycle mean plane 7C

Indeed, in the first case all substituents have bulky atoms (groups) in each *ortho*-position of the aryl ring (either methyl groups or chlorine atoms). This prevents the free rotation of substituents. In the second case, phenyl groups which have no steric restrictions for rotation are attached in all *meso*-positions. This allows the corrole molecule to form a conformer with substantially smaller dihedral angles between the planes of the phenyl groups and the macrocycle mean plane. This is consistent with the calculated values of dihedral angles θ for two corroles (see table below).

Dihedral angles values between the 7C plane and the pyrrole ring plane – φ , between the pyrrole ring plane and the N-H bond – δ , between the 7C plane and the meso-arylsubstituents plane – θ

Dihedral angle	Molecule (tautomer)		
	AB ₂ (T1)	AB ₂ (T2)	A ₃ (T1)
φ_A	19.0	19.3	15.7
φ_B	11.4	7.3	10.1
φ_C	5.6	3.9	5.9
φ_D	6.7	5.4	3.2
δ_A	4.7	18.9	8.6
δ_B	25.7	15.7	21.9
δ_C	3.1	–	2.7
δ_D	–	6.7	–
θ_{10}	76.2	77.0	34.9
θ_5	81.3	83.7	50.3
θ_{15}	88.8	89.4	61.1

Thus, it can be assumed that the degree of nonplanarity of the corrole macrocycle depends on the type of substituents in the *meso*-position.

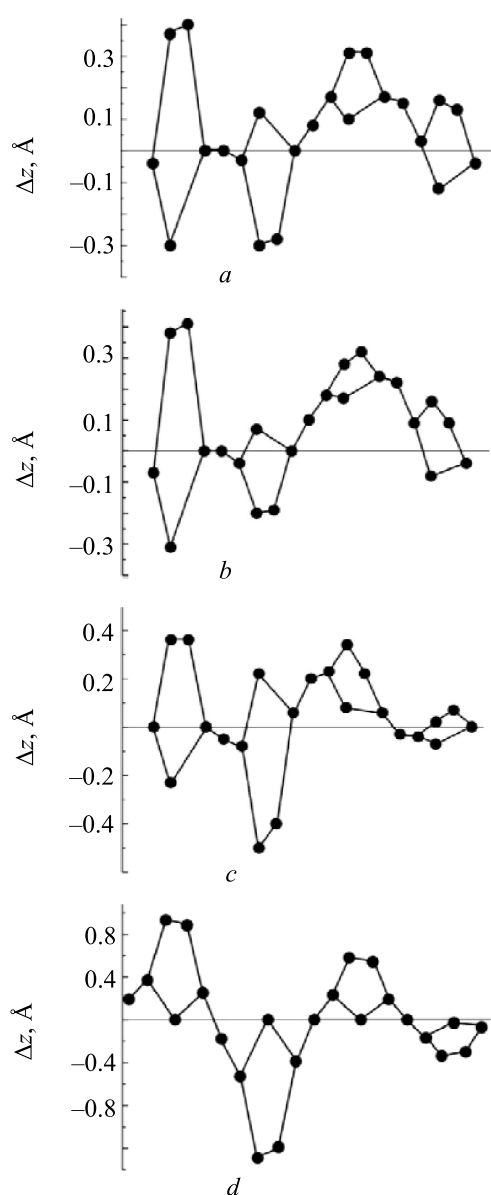


Fig. 2. Diagram of atoms deviations from the macrocycle mean plane:
 a – AB₂-corrole T1 tautomer;
 b – AB₂-corrole T2 tautomer;
 c – A₃-corrole T1 tautomer;
 d – 2,3,7,8-ethyl-5,10,15,20-phenylporphyrin.
 Pyrrole (pyrrolenine) rings A, B, C, D are shown from left to right

A comparative analysis of the dihedral angles values φ and δ , which characterize the tilt of the

pyrrole rings to the 7C macrocycle mean plane and the degree of pyramidalization of nitrogen pyrrole atoms show that the molecular conformations of the two NH tautomers have characteristic features. Thus, the dihedral angle value φ for the pyrrole rings B and C in the T1 tautomer is significantly higher than that in the T2 tautomer, while the regions of its values for the pyrrole rings A and D overlap. A characteristic feature of the molecular conformation of the T1 tautomer is a distinct pyramidalization of the pyrrole B nitrogen atom, while the A and C pyrrole pyramidalization is rather weak. Pyramidalization appears in the exposition of a proton from the plane of the pyrrole ring, characterized by δ angle. In contrast, δ angles for the A and B pyrrole rings of the T2 tautomer are comparable.

Another characteristic feature of the NH corrole tautomer molecular conformation is that asymmetric character of the macrocycle nonplanar distortions of the corrole NH tautomers (Fig. 2, a–c) is similar to the asymmetric porphyrin macrocycle distortion, in which the bulky peripheral substituents are localized at one side of a macrocycle (Fig. 2, d). Porphyrin molecule forms a *saddle*-type conformer in which all the nitrogen atoms are in the macrocycle mean plane. On the contrary, in the case of corroles, the nitrogen atoms of the pyrrole rings B, C, and D are out of the macrocycle mean plane, on the same side of it. Such molecular conformation is characterized by a *wave-like* distortion. It should be noted that the direction of the *wave-like* distortion remains unchanged during NH tautomerization.

Conclusion. The analysis of the nature of the tetrapyrrolic macrocycle nonplanar distortions of the NH tautomers of two free base 5,10,15-triarylcorroles has been carried out. Studied triarylcorroles differ by the degree of steric hindrance for the rotation of the aryl groups. It has been ascertained that both NH tautomers possess characteristic structural features. To quantify the magnitude of the nonplanar distortions of the macrocycle of corroles the $\Delta 23$ parameter has been introduced, the latter being a mean square deviation of one macrocycle atom from the 7C macrocycle mean plane. Using this approach it has been shown that $\Delta 23$ value of sterically unconstrained corroles is higher, which indicates the synergism of rotation of the aryl groups and nonplanar deviations of the skeletal macrocycle atoms, and, first of all, the tilt of the pyrrole rings relative to the macrocycle mean plane.

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