STUDY OF MOLECULAR STRUCTURE OF ALKYLATED FREE BASE CORROLES

Klenitsky D.[1], Kruk M.[1], Maes W.[2]

[1] Belarusian State Technological University, Minsk, Belarus
[2] Institute for Materials Research, Hasselt University, Diepenbeek, Belgium

Quantum-chemical calculations and steady-state spectroscopy have been applied for the study of the molecular conformation of the tetrapyrrolic macrocycle for the family of alkylated derivatives of the free base corroles. 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 □23 parameter, which is the average least-square deviation from the mean macrocycle plane 7C per one macrocycle atom. The 7C plane determined by the least-squares distances to the carbon atoms C_1, C_4, C_5, C_6, C_9, C_{16}, и C_{19} (numbering is given in according to IUPAC nomenclature) is suggested as a mean corrole macrocycle plane for the analysis of out-of-plane distortions.

It was found that all the studied compounds can be divided into four groups based on the value of the Δ23 parameter: a) Δ23 = 0.267–0.294 Å for those compounds where steric hindrances localize on th separate pyrrole rings; b) Δ23 = 0.304–0.326 Å for those, where the sterically hindered domains are formed, which consisting of two pyrrole rings; c) Δ23 =0.377–0.380 Å for those, where the one sterically hindered domain includes all three *meso*-positions of macrocycle; d) Δ23 = 0.413 Å for undecasubstituted corrole, where all the eleven alkyl groups form one sterically hindered annular domain.

The analysis of the separate structural elements characterizing the macrocycle molecular conformation demonstrates that changes of some of them parallel the Δ23 parameter trend. At the same time it was found that amplitude of the other structural perturbations does not depend on the overall degree of macrocycle distortion, but depends on the local interaction of some neighboring substituents. The two of four dihedral angles values between the pyrrole plane rings and the C_a-C_a bond length in the dipyrrole unit belong to them. The obtained correlations have been used for analysis of the spectral features of studied corroles.

References

1. Beenken W. et al. // J. Phys. Chem., A. 2014. V. 118. P. 862–871.