

INDIVIDUAL SPECTRAL-LUMINESCENT PROPERTIES OF NH-TAUTOMERS OF THE ALKYLATED DERIVATIVES OF THE FREE BASE CORROLES

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The molecular structure and spectral-luminescent properties of the 2,3,7,13,17,18-hexamethyl-8,12-di-n-buthylcorrole (H_3OAlkC) and 7,13-dimethyl-8,12-di-n-buthylcorrole (H_3TAlkC) were studied by luminescent and absorption spectroscopies in solutions in temperature range 288-328 K and quantum chemistry methods.

Absorption and fluorescence spectra of studied compounds were shown to be the superimposed spectra of two NH-tautomers. Individual spectra of tautomers were identified and the bands were assigned to the definite transitions. When comparing the results of analysis of the electronic absorption spectra of the C_b -substituted of the alkylated derivatives of the free base corroles with the interpretation of electronic absorption spectra of the C_m -aryl substituted derivatives [1], one can conclude on the differences in the electronic states ordering in these two cases. The second excited singlet S_2 state of the long wavelength tautomer T1 in both the H_3OAlkC and the H_3TAlkC lies lower than the S_2 state of the short wavelength tautomer T2, whereas in case of the C_m -aryl substituted derivatives the opposite pattern is observed: the S_2 state of the short wavelength tautomer T2 is lower than that of the long wavelength tautomer T1. It is likely that situation results from the different peripheral substitution architecture on these two cases. Two lowest occupied molecular orbitals are inverted: HOMO is « a_{2u} -like» when macrocycle has C_m -substitution and « a_{1u} -like» when it is substituted at C_b -positions. At the same time HOMO-1 is « a_{2u} -like» in case of C_b -substitution and « a_{1u} -like» in case of C_m -substitution.

The NH-tautomer equilibria in the ground S_0 and the lowest excited S_1 singlet states have been characterized. It was found that in the lowest excited singlet S_1 state of the H_3TAlkC the efficient NH-tautomerization takes place, whereas in the H_3OAlkC there was no shift in the equilibrium between two NH-tautomers. The observed difference is due to the different mutual positions of the lowest excited S_1 state in these two NH-tautomers. These energies have been calculated by addition of the transition energies, found from the experimental spectra, to the calculated ground state energies. As a result the S_1 states of two NH-tautomers of the H_3OAlkC have about the same energy, while the S_1 state of the T2 tautomer lies higher for 555 cm^{-1} compared to that of the T1 tautomer.

Based on the set of the experimental and theoretical data we have concluded that the difference in the molecular conformation account for the described above spectral and functional differences. Thus, when the macrocycle is substituted at the C_2 and C_{18} positions the macrocycle core size increases due to the steric interactions of the alkyl substituents. These interactions favor the planarization of macrocycle. On the contrary, the core size decreases when these positions are free. As a result the Δ_{23} value, which is indicative for the magnitude of nonplanar macrocycle distortions, increases. The C_1C_{19} bond length in the dipyrrole fragment of macrocycle is the marker of these interactions.

References

1. Beenken W.J.D., Presselt M., Ngo T.H. et al. Molecular Structures and Absorption Spectra Assignment of Corrole NH Tautomers // J. Phys. Chem., A. 2014. Vol. 118. P. 862-871.