COMPUTER SIMULATION OF THE FREE BASE CORROLE TAUTOMERIZATION

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Tetrapyrrolic macrocycle family has a group of contracted compounds called corroles having the direct pyrrole–pyrrole linkage. The free base corrole molecules show pronounced nonplanar distortions due to sterical hindrances imposed by three protons in the macrocycle core. Along with the radiative deactivation of the lowest singlet S_1 state and intersystem S_1-T_1 crossing, the NH tautomerization was found to be one of the channels of the excitation energy deactivation in the free base corrole [1]. The NH tautomerization was concluded to be associated with overcoming the potential barrier, therefore according to the Arrhenius equation a decrease/increase in temperature ultimately leads to a decrease/increase in the tautomerization rate. As a result, the stabilization of the short wavelength NH tautomer takes place at low temperatures, whereas two tautomers are about equally populated at room temperatures.

The direct determination of the NH tautomerization rate and elucidation of its pathway(s) is quite complicated task. At the same time there are several indirect data allowing shedding light on the NH tautomerization features. The most interesting one among them is the temperature dependence of the NH tautomerization rate. In this work to describe the NH tautomerization in the free base corroles the energy level balance equations system is developed with implementing of the experimental data sets on the temperature dependence of the tautomerization rate. The set of experimental data, consisting of the total fluorescence spectra intensities and fluorescence quantum yields measured in the temperature range from 265 to 338 K are satisfactory reproduced with the theoretical solution of the above described system of equations. The theoretical temperature dependence of the NH tautomerization rate in the lowest excited singlet state fits the experimental one.

References

1. Kruk M.M. et al. // J. Phys. Chem., A. 2012. V. 116. P. 10695–10703.