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TEMPERATURE DEPENDENCE OF THE CORROLE TAUTOMERIZATION RATE

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The family of tetrapyrrolic macrocycles 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 T2 takes place at low temperatures, whereas both T1 and T2 tautomers are about equally populated at room temperatures [1].

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 where each of two NH tautomers was represented with three energy levels with implementing of the experimental data sets on the temperature dependence of the tautomerization rate. Since the difference in the energy barriers for the T1 to T2 tautomerization and back is as small as 33cm^{-1} , the ground state populations of two NH tautomers are expected to be equal. For the simplicity of description of the lowest singlet excited states depopulation the total rate of radiative and nonradiative transitions leading to the population of the ground electronic state S_0 is accounted. For the T2 tautomer this rate is described by rate constant k_{21} and for the T1 tautomer by the rate constant k_{34} . The rate of the T2 to T1 tautomerization in the lowest singlet state is defined by constant $k_{25}(T)$, with the temperature dependence is determined by Arrhenius equation:

$$k_{25}(T) = k_{25}^0 \exp(-E_a / RT), \quad (1)$$

where E_a - activation energy, R - universal gas constant, k_{25}^0 - constant which can be approximated from experimental data. The back T1 to T2tautomerization in the lowest singlet electronic state is prohibited due to the energy difference reason. The rate constant of the T2 to T1 tautomerization in the T_1 state is designated as $k_{36}(T)$ and the back T1 to T2 tautomerization was not considered due to the energy level positioning.

It is supposed that system is excited by the short pulse at the wavelength where two tautomers absorb equally. As a result an equal population for each of the S_1 states of both tautomers T1 and T2 is achieved. In this way the initial populations $p_2(t=0)$ and $p_5(t=0)$ are equal to 0.5. The system of balance equations for the level populations corresponding to the diagonal elements of the density matrix has the form:

$$\begin{aligned} \partial p_1 / \partial t &= k_{21} p_2 + k_{31} p_3, \\ \partial p_2 / \partial t &= -k_2 p_2, \\ \partial p_3 / \partial t &= -k_3 p_3 + k_{23} p_2, \\ \partial p_4 / \partial t &= k_{54} p_5 + k_{64} p_6, \\ \partial p_5 / \partial t &= -k_5 p_5 + k_{25}(T) p_2, \\ \partial p_6 / \partial t &= -k_{64} p_6 + k_{36}(T) p_3 + k_{56} p_5, \end{aligned} \quad (2)$$

where the following designations for the rates are introduced:

$$k_2 = k_{21} + k_{23} + k_{25}(T), \quad k_3 = k_{31} + k_{36}(T), \quad k_5 = k_{56} + k_{54}. \quad (3)$$

The system of equations (2) is solved both analytically and numerically. Fluorescence quantum yield of the tautomer T1 was found to be defined by the ratio $k_{54}/(k_{54} + k_{56})$ and does not change with the temperature change, whereas that of the T2tautomer is determined by the ratio $k_{21}/(k_{21} + k_{23} + k_{25}(T))$. As a result, it was found that despite the pronounced temperature dependence for the experimental parameters alone, the total fluorescence intensity demonstrates a weak dependence on temperature. The final expression for the total fluorescence intensity I_{Σ} has the form:

$$I_{\Sigma} = \frac{k_{54}}{2(k_{54} + k_{56})} \left(1 + \frac{k_{25}(T)}{k_2} \right) + \frac{k_{21}}{2(k_{21} + k_{23} + k_{25}(T))} \frac{(k_{21} + k_{23})}{k_2}. \quad (4)$$

In summary, the 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. The probability of the tautomerization in the lowest triplet state is defined.

- [1] Kruk, Mikalai M., Unraveling the Fluorescence Features of Individual Corrole NH Tautomers / M. Kruk, T. H. Ngo, P. Verstappen, A. S. Starukhin, J. Hofkens, W. Dehaen and W. Maes // Journal of Physical Chemistry, A. - 2012. - V. 116. - P. 10695 – 10703.