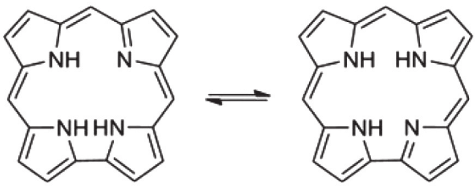
Ajeeb Y.[1,2]**, Knyukshto V.**[3]**, Karlovich T.**[1]**, Kruk M.**[1]**, Dehaen W.**[4]**, Maes W.**[5]

TEMPERATURE AND HEAVY ATOM EFFECTS ON THE FREE BASE CORROLE TAUTOMERIZATION

[1]*Belarusian State Technological University, Belarus, Minsk, e-mail: krukmikalai@yahoo.com*
[2]*Art, Sciences & Technology University in Lebanon, Beirut, Lebanon*
[3]*B.I. Stepanov Institute of Physics of National Acad. of Sci., Belarus, Minsk*
[4]*Katholieke Universiteit Leuven, Belgium, Leuven*
[5]*Insitute for Materials Research, Hasselt University, Belgium, Diepenbeek*

Corroles represent a peculiar family of contracted tetrapyrrolic macrocycles with a direct pyrrole–pyrrole linkage and the free base derivatives show pronounced nonplanar distortions due to sterical hindrances imposed by three protons in the macrocycle core. To date, studies on the excitation energy deactivation pathways in corroles have mainly focused on the radiative deactivation of the lowest singlet S_1 state, and the fluorescence spectra, quantum yields and lifetimes have been measured and discussed for a number of the free base corrole derivatives [1]. At the same time the singlet to triplet S_1–T_1 intersystem crossing was found to be the main excitation energy deactivation route in corroles as it is for most of related tetrapyrrolic macrocycles, except highly distorted compounds [2]. Recently, the individual ground state absorption and fluorescence features have been distinguished for the two NH tautomers (see Scheme 1) of the free base meso-triarylcorroles [3-6].



Scheme 1. *Two NH-tautomres of the free base corrole*

The NH tautomerization rate was found to depend strongly on the temperature [2]. 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, at low temperatures the stabilization of the short wavelength NH tautomer T2 takes place, whereas at room temperatures both T1 and T2 tautomers are about equally populated. The temperature effect is observable in the relatively narrow temperature range, in which the other intramolecular transitions can be considered as having the constant values. Therefore the study of temperature dependent equilibrium between two NH tautomers provides the possibility to estimate the NH tautomerization rate value, which is not quantified yet.

From the other side, the pronounced heavy atom effect is resulting in the decrease in the fluorescence quantum yield and increase in its deactivation rate, as well as increase in the intersystem crossing quantum yield in the free base corroles. Heavy atom effect, which does not directly concern the motion of protons in the free base corrole macrocycle core, does not influence all the intramolecular transition rates except those, related to intersystem crossing, i.e. the singlet to triplet S_1–T_1 intersystem crossing, which leads to the lowest triplet state population, and the triplet to singlet T_1–S_0 intersystem crossing, which leads to the ground state population. Thus, the main features of the heavy atom effect are the fluorescence quenching, increase in the triplet state quantum yield and decrease in the T_1 state lifetime. Since the S_1–T_1 intersystem crossing, as stated above, to be the main route of the excitation energy deactivation, its changes lead to the modulating of the competition between the intersystem crossing and NH tautomerization, which results in the changes in the equilibrium between two NH tautomers.

Finally, when the H to D isotope substitution was made in the macrocycle core (which, in fact, can be also considered as the specific heavy atom effect in macrocycle core), the NH tautomerization rate changes dramatically whereas all the other intramolecular transition rates are barely affected, if any.

The aim of given contribution is the estimation of the NH tautomerization rate based on the experimental data on the temperature dependence and the heavy atom effect on the NH tautomer equilibrium.

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