

Wrocław University
of Science and Technology

Theoretical studies of the influence of environment on photochemical and photophysical properties of selected heterocyclic compounds

by

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DISSERTATION

submitted in partial fulfillment
for the doctoral degree in

CHEMICAL SCIENCES

at the

Faculty of Chemistry

Wrocław, April, 2022

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Abstract

This doctoral dissertation is a collection of thematically coherent published articles concerning computational photochemical studies of selected heterocyclic molecules, partially supplemented by experimental results. In recent years, several scientific reports have demonstrated that the electronic structure of solvent molecules or organic substituents of chromophores can actively contribute to the photochemistry of light-activated molecules. Consequently, the nearby surroundings of chromophores can open new photorelaxation channels that cannot be observed in the gas phase. However, photochemical theoretical studies of heterocyclic compounds are often limited to molecular fragments responsible for absorbing UV photons. Therefore, the potentially active role of the chemical environment of chromophores in their photochemistry was not repeatedly considered in computational studies. The aim of this thesis was to perform quantum-chemical calculations to elucidate the influence of solvent water molecules and substituents on photochemical phenomena of heterocyclic compounds that are biologically important or relevant in the field of prebiotic chemistry. The conducted theoretical studies have indicated that solvent water molecules can enable photooxidation or photoreduction processes of UV-excited chromophores through an electron-driven proton transfer (EDPT) and water-to-chromophore electron transfer (WCET), respectively. In particular, a quantum-mechanical water molecule with the thiocarbonyl group of a chromophore can form a temporary excited-state interaction that involves lone electron pair orbitals of the thiocarbonyl sulphur and H_2O oxygen atoms, driving the WCET process. The thiocarbonyl substitution in heterocyclic compounds also allows for efficient singlet-triplet intersystem crossing, opening a pathway to the population

of long-lived triplet states. Furthermore, the ribose molecule chemically bound to a chromophore can stabilize a reactive triplet excited state, thus allowing for the hydrogen atom transfer between the ribose and nucleobase. Consequently, UV-induced inter- or intramolecular electron transfer reactions can create reactive radicals, which may damage the initial structure of chromophores or lead to desirable products that are difficult to obtain in ground-state chemistry. The significance of this dissertation is to demonstrate that photochemical phenomena are often complex processes that have to be investigated considering both the molecular structure of the chromophore and the nearby chemical environment.