

**Abstract of Agnieszka Ożóg's doctoral dissertation titled:**

**"New chemiluminogenic systems derived from the group of acridinium esters - synthesis, structure, physicochemistry, optimization for analytical applications"**

Twenty 10-methyl-9-(phenoxycarbonyl)acridinium trifluoromethanesulfonates (acridinium salts) and their acridinium precursors, 9-(phenoxycarbonyl)acridines (neutral bases) were synthesised, isolated, purified, and chemically identified.

Single monocrystals of four acridinium salts, one acridinium precursor and one related compound, were obtained and subjected to diffractometric structural analysis. Based on X-ray data and information were obtained on the molecular structure of the compounds, crystal architecture, and intermolecular interactions in the crystalline solid phase.

Electronic absorption and fluorescence spectra of 8 selected acridinium esters and the corresponding acridine precursors were recorded to determine their spectral characteristics. These characteristics disclosed unique information concerning their properties but also show that the long-wavelength UV-Vis absorption of acridinium cations only slightly interferes with the chemiluminescence generated with their participation.

Absorption vibrational spectra of 4 selected acridinium salts and their acridinium precursors were recorded, and an attempt was made to correlate the wavenumbers of selected vibrations with some of the physicochemical parameters of the studied molecules. Such correlations were found between the wavenumbers of deformation vibration of the carbonyl group (C=O) and the induction constants ( $\sigma_I$ ) of the substituents in the *ortho* position of the phenyl ring, and the stretching vibration of the carbonyl group and the partial charges on the C(9) and C(15) atoms, as well as the  $p_z$  LUMO coefficients of the C(9) atom.

Twenty-seven of the tested acridinium salts emit radiation in the visible region called chemiluminescence when subjected to reaction with hydrogen peroxide in aqueous or methanolic solutions, alkalised with inorganic (NaOH), organic (TBAOH) or Lewis (DBU) bases. The chemiluminescence of the acridinium cations present in respective salts can be of the flash or glow type and last for several – a dozen or several dozen – several hundred seconds. The efficiency/effectiveness of the chemically generated radiation emission depends on the emitter's build, the environment's nature and pH, the oxidant concentration and the experiment's time. The quantum yields of chemiluminescence of the investigated acridinium salts do not exceed  $3 \times 10^{-2}$  einstein/mol. The low level of this quantity means that most

acridinium cations are involved in "dark reactions", which do not lead to the formation of electronically excited and radiation-emitting 10-methyl-9-acridone molecules. The values of the original parameter named relative utility (RU) – taking into account the quantum yield (efficiency/effectiveness) of chemiluminescence and the stability of acridinium cations under experimental conditions – differ by up to 4 times and significantly depend on the structure of the phenyl moiety being the crucial leaving group upon chemiluminescence generation. The found nonlinear correlation of the RU with the volume of the hydration layer of phenyl carboxylate or phenolate anions released in the process of generating the radiation, draws perspectives for rational modelling acridinium chemiluminogens with expected utilitarian properties. The linear relationship between the number of emitted photons and the concentration of chemiluminogenic salts falls in the range of  $10^{-10}$ – $10^{-5}$  M, disclosing the possibilities of using the investigated acridinium cations in analytics.