Synthesis of aromatic polycyclic N-ethoxycarbonylthioamides and their use in the synthesis of new fluorophores

Thioamides are useful building blocks in the synthesis of heterocyclic compounds. Of particular interest in this respect are thioamides having an ester group bound to the nitrogen atom, R(C=S)NHCOOEt.

Previous work carried out at the Department of Organic Chemistry, Faculty of Chemistry, University of Łódź, has shown that these compounds can be used as pronucleophiles in the Mitsunobu reaction and substrates in the new method of 4-hydroxythiazole synthesis. The pyrenyl derivatives of this heterocyclic system obtained by this method showed strong and environment-dependent fluorescence.

The subject of this doctoral thesis is a continuation of this research trend. It concerns the development of a method of synthesis by Friedel-Crafts type reactions of arenes with ethoxycarbonyl isothiocyanate, *N*-ethoxycarbonylthioamides derivatives of selected polycyclic aromatic hydrocarbons.

Compounds of this type have been used in the synthesis of derivatives exhibiting strong fluorescent properties. Particular emphasis was placed on the derivatives of the well-known fluorophores - pyrene and perylene. It has been shown that the thioamides can be oxidized to the corresponding *S*-oxides (aminosulfines), Ar(C=S=O)NHCOOEt. These compounds, in a strongly acidic medium (trifluoromethanesulfonic acid), surprisingly underwent cyclization leading to annulation of the 2-iminothiophene ring.

It was also shown that the obtained *N*-ethoxycarbonylthioamides can be used, using methodology previously described in the Laboratory, for the synthesis of pyrenyl- and perylenyl-4-hydroxythiazoles and 4-thiazolinones containing ester groups.

N-ethoxycarbonylthioamides and their *S*-oxides did not show fluorescent properties, while the remaining compounds were strong emitters. Studies of their basic photophysical properties have been carried out (absorption and emission spectra in various solvents, quantum yields of emission).

It is noteworthy that one of the obtained compounds showed a rarely observed white light emission. It was explained that the reason for this phenomenon is the transfer of a proton to a solvent molecule (DMSO) taking place in the excited state (ESPT, Excited-State Proton Transfer).