THERMODYNAMIC STUDY ON TRIAZOLO-TRIAZOLE HETEROCYCLIC SYSTEMS

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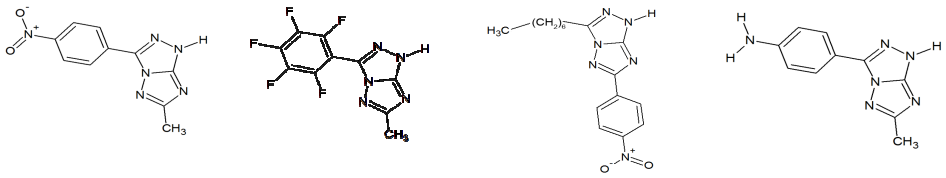
Extensive replacement of carbon by nitrogen in aromatic heterocycles can be used not only for the tuning of electronic and structural features of the compounds but, depending on their structure, also for inducing totally new features such as N-H acidity and coordination ability to metal sites. Those features can be potentially relevant not only for biological applications, but also in the field of advanced materials [1,2]. Acid-base properties and complex formation with metal ions of four new triazolo[3,2-c]triazoles (Scheme) having substituents of different electronic character on the bicycle have been investigated at 25 °C in NaCl 0.5 M, as ionic medium, by using potentiometry, polarography and UV-Vis spectrometry (absorption and emission). The pH investigated spans between 0.5 and 12.



The study indicated that the neutral heterobicycle (HL) has acid-base properties strongly influenced by the presence of electron withdrawing or releasing groups at position 7 (it can deliver the H^+ to form the conjugated base L^- and can accept up to two protons, forming the species H_2L^+ and H_3L^{++}). By varying the groups attached at the heterocycle, a remarkable shift of pKa values, up to 5–6 units, is observed. The formation of the cationic species is accompanied by complex tautomeric switchings as shown by single crystal X-ray analysis and theoretical calculations [3,4]. The excited-state proton transfer also is influenced by the presence of electron withdrawing or releasing groups at position 7. Evidence of the formation of Me(II)-HL, mononuclear complexes, has also been obtained.

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