Thermochromism in Crystals and Co-Crystals – A Quantum Chemistry Insight

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Photochromic and thermochromic compounds are widely studied because of their potential applications in sensing devices. Still, most of these studies rely on characterizations performed in solutions whereas there is a need for understanding and optimizing their properties in the solid state. Salicylideneanilines (or anils), which are characterized by a tautomer equilibrium, between an enol and a keto form of different colors, present remarkable thermochromic and photochromic properties [1-2]. The enol form is usually the most stable but appropriate choice of substituents and conditions (solvent, crystal, host compound) can modify the thermodynamics and kinetics of the transformation [3]. One strategy to optimize the switching behavior and the related optical properties consists in forming co-crystals. In this presentation we discuss the quantum chemistry components of a multidisciplinary approach, which also includes synthesis of the chromophores, crystal formation, and physico-chemical characterizations. In particular, our latest achievements towards describing the structure-property relationships of co-crystals of anils with co-formers (featuring H-and X-bonding interactions) will be discussed. This encompasses i) the prediction of the crystal structures and of the key geometrical parameters, ii) the evaluation of the relative energy of the different keto and enol forms, iii) the simulation of the NMR signatures, to help in determining the enol-keto equilibrium constant in the solid state, and iv) the prediction of the UV/visible absorption spectra. In all cases, the focus is set on analyzing the effects of the interactions in the solid state between the chromophore and the co-former. Different methods are employed, from embedding techniques to periodic boundary conditions approaches. Compounds from the anil family (see Figure) are selected to illustrate these issues, owing to the availability of experimental data [4].

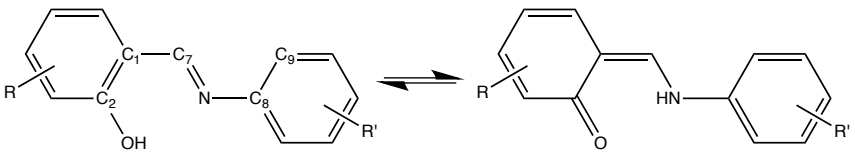

Figure. General structure of the anil derivatives. The compounds under investigation are (E)-2-methoxy-6-(pyridine-3-yliminomethyl)phenol, N-(5-chloro-2-hydroxybenzylidene)-aniline, and N-(5-chloro-2-hydroxybenzylidene)-hydroxyaniline

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