Keto Forms in Schiff Bases of Salicylaldehydes: Structural and Theoretical Aspects

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Schiff Bases of Salicylaldehydes undergo enol-keto tautomerism involving proton transfer from the hydroxylic oxygen to the imino nitrogen atom [1]. The difference in molecular conformation (planar and non-planar for thermochromic and photochromic compounds respectively) and the resulting different crystal packing has been considered crucial for the chromobehaviour of N-salicylideneanilines. In contrast, studies of N-salicylidenealcylamines suggested that the electron density on the imine N-atom is what is crucial to thermochromism, rather than molecular planarity, which on the other hand is detrimental to photochromism. It is natural therefore, to suppose that by influencing the electron density on the N-atom by substitution in the salicylaldehyde or/and the amine moiety of the molecule, keto or enol forms of the compounds may be observed. However, no stable keto form had been observed in the crystalline state so far among the substituted N-salicylideneamines and therefore it has not been characterised structurally. In the present study we report the first structural characterisation in the crystalline state of the *cis*-keto form of a number of N-salicylideneamines, which derive from methoxy substituted salicylaldehydes and aliphatic amines. Moreover, we compare it to the theoretical results derived from DFT quantum mechanical calculations in an attempt to understand the important characteristics that render the *cis*-keto form more stable for certain derivatives in this class of N-salicylideneamines.

[1] Hadjoudis E., Mavridis I. M., *Chem. Soc. Rev,*. 2004, **33**, 579.

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