

Solvent-free mechanosynthesis and thermochromic properties of *o*-hydroxy Schiff bases

Marija Zbačnik and Branko Kaitner

Laboratory of General and Inorganic Chemistry, Department of Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102a, HR-10002 Zagreb, Croatia.
mzbacnik@chem.pmf.hr

o-Hydroxy Schiff bases are a long time known group of photochromic and thermochromic organic compounds.^{1–3} The structural reason for a colour change upon UV-irradiation or the change of temperature is the electron density alteration in the region of the C=N imino group followed occasionally by the change of molecular planarity.² The state of electron density in the six-membered pseudo-aromatic chelate ring determines the position of the hydrogen atom in the intramolecular O–H···N or N–H···O hydrogen bond and the ratio of the tautomers.³ A recent study has revealed that the fluorescence plays a crucial role in the solid-state thermochromism of *o*-hydroxy Schiff bases on the temperatures below the room temperature when the fluorescence is much stronger than on the temperatures above room temperature.⁴ Much of interest on the other hand has been devoted to neat grinding (NG) and liquid-assisted grinding (LAG) since these synthetic routes have proven to be fast and environmentally more acceptable but also successful.⁵

To obtain a better insight into chromic properties of *o*-hydroxy Schiff bases, four thermochromic Schiff bases derived from salicylaldehyde and its derivatives and different aromatic amines have been synthesized by means of NG and LAG. The crystal and molecular structures were obtained using the single crystal X-ray diffraction performed at RT and LT. Solid products obtained by NG and LAG were characterized by DSC and X-ray powder diffraction and compared with the data of recrystallized material.

The thermochromic properties of the synthesized Schiff bases were studied using XRD giving quantitative insight into the diverse colorization upon intramolecular proton transfer changes, tautomer equilibriums and molecular planarity.

References

- [1] Cohen, M.D. & Schmidt, G.M.J., (1962) *J. Phys. Chem.* **66**, 2442–2445.
- [2] Hadjoudis, E., Vittorakis, M. & Mavridis, I.M., (1987) *Tetrahedron* **43**, 1345–1360.
- [3] Ogawa, K., Kasahara, Y., Ohtani, Y. & Harada, J., (1998) *J. Am. Chem. Soc.* **120**, 7107–7108.
- [4] Harada, J., Fujiwara, T. & Ogawa, K., (2007) *J. Am. Chem. Soc.* **129**, 16216–16221.
- [5] James, S. L., Adams, C. J., Bolm, C., Braga, D., Collier, P., Friščić, T., Grepioni, F., Harris, K.D.M., Hyett, G., Jones, W., Krebs, A., Mack, J., Maini, L., Guy Orpen, A., Parkin, I.P., Shearouse, W.C., Steedk, J.W. & Waddelli, D.C., *Chem. Soc. Rev.* DOI: 10.1039/c1cs15171a.