Polymorphism and Photochromism of Salicylideneaniline, Frédéric Arod,[a*] Manuel Gardon,[a] Philip Pattison[b] and Gervais Chapuis[a], [a]*LCr1, BSP, EPFL, 1015-Lausanne, Switzerland, and* [b]*SNBL, ESRF, Grenoble, France, Metropolitan*. E-mail: frederic.arod@epfl.ch

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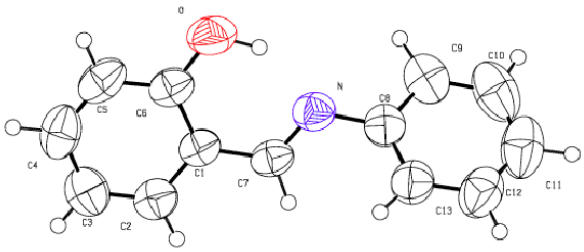
Organic compounds exhibiting photo- or thermochromicity have been of considerable interests owing to their properties and possible applications. The photochromism of salicylideneaniline (SA) was discovered by Senier *et al*. at the beginning of last century. In 1964, Cohen *et al*. observed polymorphism [1] and indicated that the colour change was not accompanied by any observable changes in X-ray diffraction pattern and infrared spectrum. Destro *et al*. [2] gave a possible solution of the structure of the α1-polymorph, but could not go further due to the lability of the irradiated product. It is generally accepted that the stable form of SA in the ground state is the enol form, with an intramolecular hydrogen bond between the hydroxyl group and the nitrogen atom. Upon photoexcitation of this enol form with UV light, it undergoes an ultrafast proton transfer from the hydroxyl group to the nitrogen, due to the electronic redistribution in the excited state. The proton transfer generates a keto tautomer in the excited singlet state. However, the details of the structure configuration give rise to controversy between a cis and a trans form in which the oxygen and the imine hydrogen atom will be in cis or trans configuration with regard to the C1-C7 bond [3]. Here, we report for the first time, on the α2-polymorph structure of SA in the ground state, already mentioned by Cohen. Then, we revisit the α1-polymorph structure of SA described by Destro, but reconsidering his hypothesis. We suggest a lowering of the symmetry from orthorhombic to triclinic with the aim to remove the ambiguity of the two-fold axis and improve the structure solution. Spectroscopic measurements on both modifications reveal characteristic changes in absorption spectrum during irradiation.



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