Polymorphism Dependent Crystalline Photochromism of Salicylideneanilines

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Some salicylideneanilines show crystalline-state photochromism. The reversible color change from yellow to red upon irradiation by UV light is the result of the photo-isomerization from the enol to the *trans*-keto form, which is explained as an intra-molecular proton transfer followed by a crank-shaft-motion type conformational change. The red-colored crystal fades to yellow by a thermal process.

The salicylideneaniline derivative *N*-3,5-di-tert-butylsalicylidene-3-carboxyaniline has three polymorphs: the α phase (pale yellow needle), the β phase (yellow plate), and the γ phase (orange block). Only the α and β forms are photochromic, whereas the γ form is thermochromic. X-ray crystal structure analyses of these three forms revealed the significant differences in dihedral angles in these molecules. The large dihedral angle in the α and β forms makes the enol conformation (yellow) unstable, which explains why the yellow to red photochromic reaction occurs easily.

In order to investigate the large difference in the lifetime of the red *trans*-keto conformation in the α (17min.) and β forms (780min.), the crystal structure of the irradiated (red-colored) crystal was analyzed. Newly established inter-molecular hydrogen bonds were observed in this red-colored β form but not in the red-colored α form. This result indicates that the inter-molecular hydrogen bond is stabilizing the red *trans*-keto conformation and preventing it from converting to the yellow enol conformation.

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