



A different photo-sensitivity of isostructural crystals of *N*-(3,5-dihalosalicylidene)-2,6-dimethylaniline analogues: search for the definite reaction room in the crystal to exhibit photochromism

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ABSTRACT

Photo-sensitivity and X-ray crystal structure of three *N*-(3,5-dihalosalicylidene)-2,6-dimethylaniline analogues were determined to reveal a definite space maintained in the photochromic crystals.

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Crystal engineering, which is defined as the understanding of intermolecular interactions in the context of crystal packing and in the utilization of such understanding in the design of new solids with desired physical and chemical properties,¹ is one of the most important fields in recent chemistry and physics.² Thus, understanding the structure of certain organic compounds in the solid state is critical to the engineering of physical properties for new technologies. Photochromic molecules, which can switch reversibly between two forms by excitation using appropriate wavelength of light, have potential applications for photo-electronic devices such as optical memory and switches.³ One type of the well-known example is *N*-salicylideneaniline and its derivatives (Schiff bases), whose photochromic behavior contains photo-induced alteration of molecular structure based on inherent enol-keto tautomerism.^{4,5} For non-photochromic Schiff base crystals, structural demands prohibit molecules from such photo-induced alteration in a restricted room in the crystal.⁶ Physicochemical properties of crystalline compounds are connected to topochemical effects;⁷ thus, analogous Schiff bases with the same topology have been suggested to have similar photochromic properties. Contrary to this generally accepted concept, we found that certain isostructural Schiff bases exhibited different photo-sensitivity. In this Letter we report photo-sensitivity and X-ray crystal structure

of three *N*-(3,5-dihalosalicylidene)-2,6-dimethylanilines **1–3** for a better understanding of the reaction room in the crystal state.

All the Schiff bases were prepared by the usual condensation of 3,5-dihalosalicylaldehydes with 2,6-dimethylaniline.⁸ Irradiation to the yellowish crystalline **1** with 365 nm light produced a photo-colored orange species that showed an absorption band with a maximum at around 520 nm. The solid state reflectance spectra of **1** before and after UV light irradiation are shown in Figure 1. In the case of compounds **2** and **3**, however, the crystals did

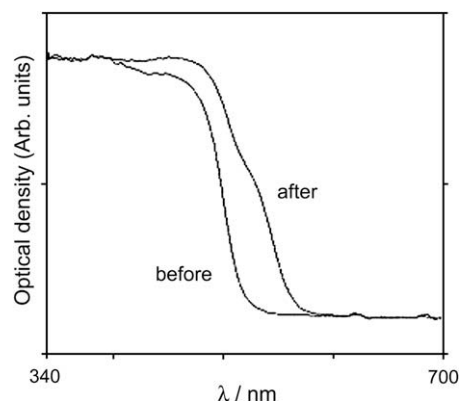


Figure 1. Reflectance spectra of **1** before and after UV irradiation.

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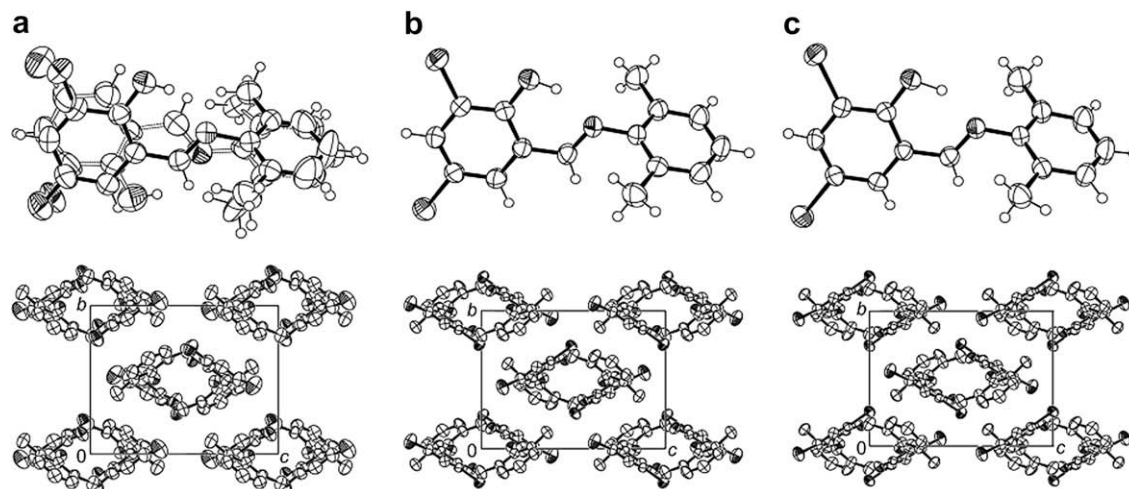


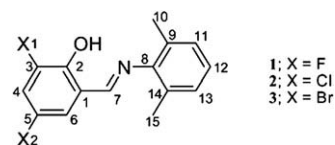
Figure 2. Crystal structure of **1**(a), **2**(b), and **3**(c). The thermal ellipsoids are drawn at the 50% probability. Above: ORTEP drawings of unimolecular structure; bottom: packing diagrams along the *a* axis. In respect to the disordered structure of **1**, the bonds of the major (**1A**) and minor (**1B**) components are drawn by the fill and open lines, respectively. **1B** is not shown in the packing diagram for clarity.

not show such photo-coloration in spite of the similarity of their reflectance spectra to those of **1** before photo-irradiation.

In order to discuss the relationship between the photo-sensitivity and structure for these Schiff bases, X-ray crystallographic analyses of **1** and **3** were carried out at room temperature. We have already determined the crystal structure of **2**.⁹ The molecular structures and packing diagrams of **1–3** are shown in Figure 2.¹⁰

From the X-ray structural studies two important features became apparent. One is that photochromic Schiff base **1** takes almost the same molecular geometries or packing modes as those of non-photochromic **2** and **3**. The similarity of the crystal structure is ascribed to the same orientation of molecular polarity and analogous dispersion forces based on a common molecular formula with different halogen substituents. The aniline ring of each Schiff base is twisted out of the salicylidene plane due to steric repulsion between the azomethine hydrogen and the methyl substituents. Dihedral angles between the least-square's planes defined by the salicylidene ring and the aniline rings are 65.47° for **1** (major component **1A**, vide infra), 63.51° for **2**, and 63.62° for **3**, respectively. The centrosymmetric counterparts of the twisted molecule are arrayed along the *a* axis to construct one-dimensional columns.

Another point is more important. The crystal lattice of photochromic **1** contains a disordered minor component, whose occupancy factor is calculated to be 15%. The minor component **1B** is expressed as a flip-rotated form of coexisting major component **1A** at the same position. This appearance is different from the dynamic disorder observed in the crystals of stilbenes and azobenzenes which undergo *E–Z* isomerization of C=C or N=N bonds.¹¹ Although the disordered structure bears a striking resemblance to that of a photo-colored Schiff base reported by Ohashi et al.,¹² **1B** is not generated photochemically. In the literature, it was emphasized that two-photon excitation by 730 nm radiation was very important to observe the photo-induced structural change of organic crystals. Under natural light, photoreaction might take place only near surface of the crystals. As a matter of course, we could not image any type of *trans*-keto structure from the electron density peaks by X-ray analysis. In view of the positions of oxygen atoms with respect to other atoms for two components, **1A** cannot be transformed into **1B** via the so-called pedal motion of two aromatic rings. Therefore, it is obvious that the disordered components exist statically in the crystal lattice when the crystal forms. In the non-photochromic crystals **2** and **3**, no disordered structure was detected at all.



Scheme 1. Schiff bases studied.

Although these crystals are formed in the same packing manner, only fluoro analogue **1** possesses a little opening around the halogen atom due to smaller size of fluorine than that of chlorine and bromine. The nearest X1–C2* intermolecular distances, where the numbering of atom (X = halogen) is shown in Scheme 1 and * designates a symmetry operation of $(-x, -y, -z)$, were 3.437 Å for **1A** (X = F), 3.590 Å for **2** (X = Cl), and 3.696 Å for **3** (X = Br), respectively. The effective open spaces, which are estimated by subtracting the sum of van der Waals radii of each halogen atom and aromatic ring from the X1–C2* distances, are 0.27 Å, 0.14 Å, and 0.15 Å, respectively. These values suggest that the void space of crystal **1** is only 0.12 Å wider than that of non-photochromic **3**. Such a delicate space in the crystal of **1** might allow the molecules to be disordered in the crystal. Photo-induced alteration of the molecule is also possible in such an open room of the crystal, which can exhibit photochromism.

By the difference in photo-sensitivity of the isostructural Schiff bases, we could confirm the extraordinary importance of crystal packing perturbation for the appearance of photochromic character. On the other hand, crystal packing mode favorable for exhibiting photochromism might cause disorder of molecules in the crystal. This observation is a point to be considered for the development of organic crystal engineering.

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 - Experimental data for **1**: yield: 360 mg (69.0%). Mp: 98.0–98.5 °C. (Found: C, 68.79; H, 5.07; N, 5.35. $C_{15}H_{13}F_2NO$ requires C, 68.96; H, 5.01; N, 5.35.) δ_H (270 MHz; $CDCl_3$): 2.20 (6H, s, CH_3), 6.88 (1H, ddd, J_{ortho} 6.9, J_{meta} 3.0, J_{para} 2.0, 6'(H)), 6.99–7.13 (4H, m, 3(H), 4(H), 5(H), 4'(H)), 8.26 (1H, s, $CH=N$), 13.16 (1H, br s OH). The compounds **2**¹⁵ and **3**⁹ were reported in the literature.
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