

# Solid-State Thermochromism Studied by Variable-Temperature Diffuse Reflectance Spectroscopy. A New Perspective on the Chromism of Salicylideneanilines

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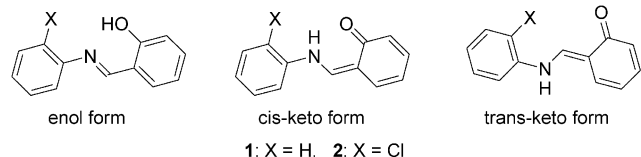
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This paper reports a successful application of variable-temperature diffuse reflectance spectroscopy for the study of the solid-state thermo- and photochromism of salicylideneanilines, which belong to a class of the most well-known chromic organic compounds. This study disproves fundamental aspects that have been widely accepted for as long as 40 years and provides a new perspective on the chromism. The enol form of salicylideneaniline, which has been wrongly regarded as pale yellow, is in fact colorless, and the pale yellow is due to a trace of the cis-keto form, which is in equilibrium with the enol form. The phototransformation from the cis-keto to the trans-keto form was observed for the first time. Although it has been accepted that a given modification of salicylideneanilines is either photochromic or thermochromic but not both, this study reveals that such an exclusive property on the chromism does not exist and that salicylideneanilines are generally thermochromic in the solid state, whether they are photochromic or not. This study demonstrates that the color of materials is controlled by a trace of colored species and that the variable-temperature diffuse reflectance spectroscopy is quite an effective tool for its detection and therefore for the study of the chromism in the solid state.

## Introduction

A reversible color change with variation of temperature is known as thermochromism.<sup>1</sup> Thermochromism is usually caused by a shift of equilibrium between chemical species of different colors due to variation in temperature. To determine the relationship between color change and shift of the equilibrium, it is necessary to measure the variable-temperature UV–vis absorption spectra. This is straightforward for compounds in solutions, but not for powdered materials. To obtain the absorption spectra of powdered materials, diffuse reflectance spectra must be measured. It has been shown that diffuse reflectance spectra resemble absorption spectra when the spectra are presented in terms of the Kubelka–Munk function.<sup>2</sup> However, there have been only a few reports on the measurement of diffuse reflectance spectra below room temperature.<sup>3</sup>

In this study, we successfully measured the diffuse reflectance spectra at temperatures between 298 and 80 K using a cryostat with a homemade sample holder, and obtained temperature-dependent UV–vis Kubelka–Munk spectra of crystalline powders of salicylideneaniline (**1**, abbreviated SA) and one of its analogues (**2**), which belong to a class of the most well-known thermochromic and photochromic organic compounds.<sup>4–10</sup> The measurements give us a new perspective on the chromism of SAs in the solid state.



The crystals of SAs have been classified into two types: one is orange and the other is pale yellow.<sup>6–8</sup> Orange crystals are

thermochromic; they become paler at lower temperatures. The thermochromism is ascribed to the shift of tautomeric equilibrium between enol and cis-keto forms,<sup>9,11</sup> with variation of temperature; the cis-keto form has an absorption band in the visible region, which decreases in intensity as the temperature is lowered. On the other hand, pale yellow crystals are photochromic; when the crystals are irradiated with UV light, they turn red; when they are left in the dark or irradiated with visible light, they revert to the original color. The photochromism is due to the reversible transformation between enol and trans-keto forms;<sup>10,11</sup> upon UV irradiation, excited-state intramolecular proton transfer proceeds to give a cis-keto form, and a subsequent geometric change produces a trans-keto form.

Extensive studies have been carried out on the photochromism of SAs.<sup>6,8</sup> According to these studies, the photochromic crystals contain only the enol form before UV irradiation. Thus, it has been assumed that the pale yellow color is due to the enol form and that the photochromic crystals are not thermochromic.

In this study, we discovered that the photochromic crystals are also thermochromic and that the yellow becomes paler as the temperature is lowered. The variable-temperature diffuse reflectance spectra revealed that a trace of the cis-keto form, the  $\lambda_{\text{max}}$  of which is different from that of the trans-keto form, exists in the crystals at room temperature, and that the cis-keto form almost disappears at low temperatures. These results lead to the conclusions that the enol form, which has been wrongly regarded as pale yellow, is actually colorless, and that the pale yellow is due to a trace of the cis-keto form.

## Experimental Section

**Materials.** Salicylideneanilines **1** and **2** were prepared according to standard procedures and recrystallized from methanol. Melting points were determined using Yanaco MP-

S3: **1**, 50.8–51.0 °C (51 °C<sup>8</sup>); **2**, 81.5–82.0 °C (83 °C<sup>8</sup>). The crystals of **1** and **2** were each ground using an agate mortar and pestle. X-ray powder diffraction of the powdered crystals was measured using a Rigaku MultiFlex powder diffractometer and it was confirmed that the diffraction pattern of each powdered crystal agrees with the patterns calculated from each of the crystal structures of the photochromic crystals.<sup>12</sup> For the calculations of the diffraction pattern, the Crystallographica package (Oxford Cryosystems, Oxford, UK) was used.

**Measurements.** Diffuse UV–vis reflectance spectra were measured on a Jasco V-550 spectrometer equipped with an integrating sphere accessory at temperatures between 80 and 298 K, using a liquid nitrogen bath cryostat Oxford Optistat DN-V with a homemade sample holder. The temperature was held constant within  $\pm 0.1$  K during the measurement.

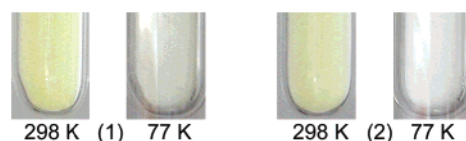
The powdered crystals of **1** and **2** (ca. 300 mg) were each packed into the sample holder. The sample holder was placed in the sample space of the cryostat. The cryostat was covered with a dark cloth and the sample space was evacuated using a diffusion pump for a few hours. During the evacuation in the dark, the trans-keto form, which might have been produced by exposure to room light during handling, decays to the enol form. To eradicate the trans-keto form, which might still be present in the sample, the sample was irradiated with a mercury–xenon lamp ( $\lambda > 560$  nm, see below) for a few minutes before the measurement of the diffuse reflectance spectra. It was confirmed that the trans-keto form is not produced by the measurement of the diffuse reflectance spectra.

To obtain the Kubelka–Munk spectra, dry NaCl powder was used as diluent of the powdered sample crystals, and NaCl (MERCK Suprapur) was ground and dried at 150 °C for 12 h under the reduced pressure before use. In a glovebag filled with nitrogen gas, the ground crystals (1 mg) and the NaCl powder (1 g) were placed in a glass vial and mixed together by rolling and shaking the vial by hand. Then, the sample was packed into the sample holder in the glovebag. The sample holder was placed in the sample space of the cryostat; the sample space was evacuated in the dark; and the sample was irradiated with a mercury–xenon lamp for a few minutes before the measurement of the spectra. Because sample crystals are slightly fluorescent, a short wave pass ASAHI Spectra SU0500 filter was placed before the detector to eliminate fluorescence from the spectra.

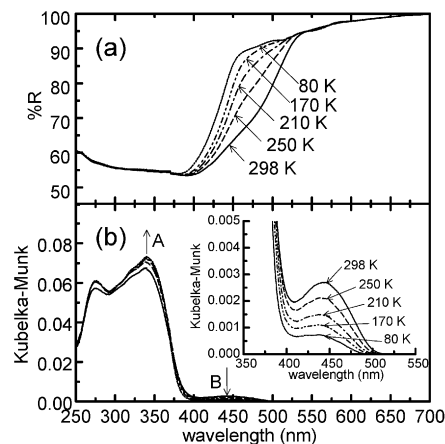
**Photoirradiation.** For the irradiation with 365- and 436-nm light, a UV–vis photoirradiation SAN-EI UVF-352S apparatus having a 350-W high-pressure mercury lamp and a fiber-optic waveguide was used. The mercury emission line of 365 nm was isolated by passing the excitation light through a band-pass HOYA U360 filter and an ultraviolet transmitting HOYA UV34 filter. The mercury emission line of 436 nm was isolated by the use of a band-pass ASAHI Spectra MX0436 filter and a heat-absorbing HOYA HA50 filter. For the irradiation with visible light, an irradiation SAN-EI UVF-203S apparatus having a mercury–xenon lamp and a fiber-optic waveguide was used. Visible light with a wavelength longer than 560 nm was isolated by the use of a sharp-cut HOYA O56 filter and a heat-absorbing HOYA HA50 filter.

## Results and Discussion

As shown in Figure 1, the photochromic crystalline powders of **1** and **2** are pale yellow at 298 K. When the temperature is lowered, the color of the powders becomes much paler and almost colorless at 77 K. The color change is reversible.



**Figure 1.** Photographs of the photochromic crystalline powders of salicylideneaniline (**1**) and 2-chlorosalicylideneaniline (**2**) at 298 and 77 K.



**Figure 2.** (a) Diffuse reflectance spectra of the photochromic crystals of salicylideneaniline (**1**) at different temperatures. (b) The Kubelka–Munk spectra of the photochromic crystals of **1** in NaCl (0.1 wt %) at different temperatures.

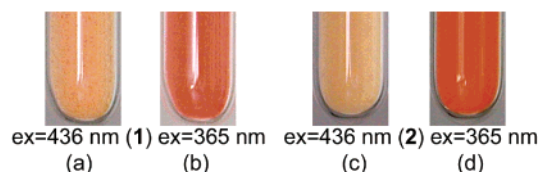
Figure 2a shows variable-temperature diffuse reflectance spectra of the powder of **1**. The spectra seem to reflect the color change. The reflectance decreases considerably in the wavelength shorter than 540 nm at 298 K. As the temperature is lowered, the reflectance increases between 540 and 380 nm. The results suggest that the powder absorbs visible light in this region and that the absorbance decreases with lowering temperature.

To relate the thermochromism with a change in absorption spectra, variable-temperature reflectance spectra were measured for the samples in which the powder is diluted with sodium chloride (concn of **1** is 0.1 wt %) and converted into the absorption spectra by the Kubelka–Munk transformation (Figure 2b). The Kubelka–Munk spectra at 298 K exhibit a strong absorption band with  $\lambda_{\text{max}} = 340$  nm, band A, and a much weaker absorption band with  $\lambda_{\text{max}} = 443$  nm, band B. Band A is assigned to the enol form, because the  $\lambda_{\text{max}}$  is nearly equal to that of the enol form in hydrocarbon solutions:  $\lambda_{\text{max}} = 338$  nm in isopentane at room temperature.<sup>13</sup> The presence of band B in Kubelka–Munk spectra of the powder samples makes a sharp contrast with the absence of band B in absorption spectra of the hydrocarbon solutions at 297 K, which exhibit no absorption at the wavelength longer than 417 nm.<sup>13</sup>

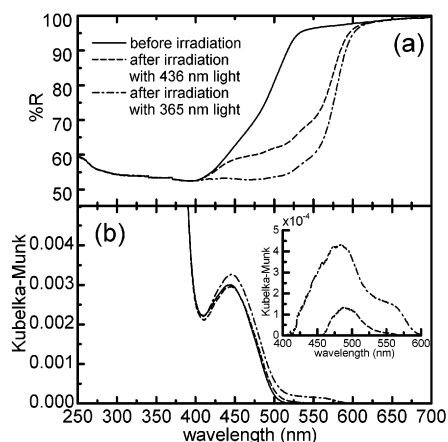
Band B is assigned to the cis-keto form on the basis of the following facts. (i) The  $\lambda_{\text{max}}$  of band B (443 nm) is comparable with that of the cis-keto form:  $\lambda_{\text{max}} = 434$  nm in methanol at room temperature<sup>14</sup> and 426 nm in isopentane at 120 K.<sup>13</sup> (ii) Band B cannot be assigned to the trans-keto form because the  $\lambda_{\text{max}}$  of band B is much shorter than that of the band of the trans-keto form (500 nm).<sup>8</sup>

When the temperature is lowered, band A increases and band B decreases in intensity. The presence of an isosbestic point at 375 nm clearly indicates that there is an equilibrium between the enol and cis-keto forms in the crystals of **1**.

When band B is irradiated at 436 nm at room temperature, the powder turns pale red (Figure 3a). The color is similar to that of the trans-keto form, which is produced by the irradiation

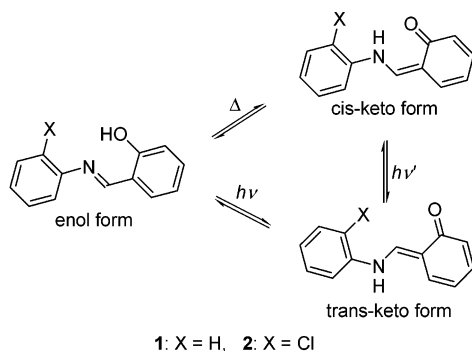


**Figure 3.** Photographs of the photochromic crystalline powders of salicylideneaniline (**1**) and 2-chlorosalicylideneaniline (**2**) after irradiation at 436 and 365 nm at 298 K.

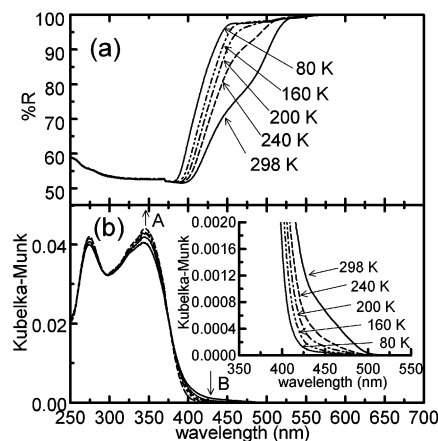


**Figure 4.** (a) Diffuse reflectance spectra of the photochromic crystals of salicylideneaniline (**1**) at room temperature before and after irradiation at 436 nm. (b) The Kubelka–Munk spectra of the photochromic crystals of **1** in NaCl (0.1 wt %) at 298 K before and after irradiation at 436 nm. The inset represents the difference after and before irradiation.

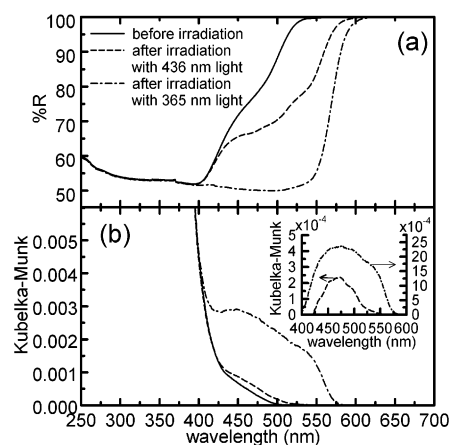
#### SCHEME 1



of band A (Figure 3b). In accordance with the color change, the reflectance considerably decreases in the region from 620 to 420 nm (Figure 4a). The reflectance spectrum resembles that of the trans-keto form. These results suggest that the irradiation of the cis-keto form generates the trans-keto form. This is confirmed by the Kubelka–Munk spectra of the diluted sample (Figure 4b). The irradiation of band B causes a slight but significant increase in intensity in the wavelength longer than 450 nm. The difference spectrum shows an absorption band with  $\lambda_{\max}$  of 487 nm. This band is unambiguously assigned to the trans-keto form, because it agrees in both  $\lambda_{\max}$  and shape with that of the trans-keto form produced by the irradiation of band A. This is the first observation of phototransformation from the cis-keto to the trans-keto form and reveals that the photoinduced colored species, the trans-keto form, is produced not only from the excitation of the enol form with UV light, but also from that of the cis-keto form, which exists only slightly in the crystals, with visible light (Scheme 1).



**Figure 5.** (a) Diffuse reflectance spectra of the photochromic crystals of 2-chlorosalicylideneaniline (**2**) at different temperatures. (b) The Kubelka–Munk spectra of the photochromic crystals of **2** in NaCl (0.1 wt %) at different temperatures.



**Figure 6.** (a) Diffuse reflectance spectra of the photochromic crystals of 2-chlorosalicylideneaniline (**2**) at room temperature before and after irradiation at 436 nm. (b) The Kubelka–Munk spectra of the photochromic crystals of **2** in NaCl (0.1 wt %) at room temperature before and after irradiation at 436 nm. The inset represents the difference after and before irradiation.

The pale red crystals turn colorless gradually when they are left in the dark at room temperature. They also turn colorless when they are irradiated with visible light ( $\lambda > 560$  nm). In accordance with the color change, band B disappears in the Kubelka–Munks spectra. Thus, the phototransformation from the cis-keto to the trans-keto form is reversible.

The photochromic crystalline powder of **2** also gave similar results. As shown in Figure 5, the reflectance decreases considerably in the wavelength shorter than 540 nm at 298 K. As the temperature is lowered, the reflectance increases between 540 and 380 nm. The Kubelka–Munk spectra of the diluted sample at 298 K exhibit a strong absorption band with  $\lambda_{\max}$  of 343 nm, band A, and a much weaker absorption band, band B, at the wavelength between 420 and 500 nm. When the temperature is lowered, band A increases and band B decreases in intensity. There is an isobestic point at 376 nm, indicating the presence of an equilibrium between the enol and cis-keto forms also in the crystals of **2**.

When band B is irradiated at 436 nm at room temperature, the powder turns pale red (Figure 3c). The color is similar to that of the trans-keto form (Figure 3d). The diffuse reflectance and the Kubelka–Munk spectra, which are shown in Figure 6,



clearly indicate the occurrence of the phototransformation from the cis-keto to the trans-keto form in the crystals of **2** (Scheme 1).

The powder of **1** is pale yellow before irradiation and red after irradiation. Thus, the colors are easily perceived. However, the intensity of the corresponding absorption band in the Kubelka–Munk spectra is very weak. In particular, the intensity of the band that emerges after the irradiation with 436-nm light is at the limit of detection (Figure 4b). This clearly demonstrates that only a trace of colored species that are likely overlooked in absorption spectra can determine the color of materials.

Although the color change with variation of the temperature is visually evident for the photochromic crystals of **1** and **2**,<sup>15</sup> Cohen and co-workers classified them as nonthermochromic based on their spectroscopic criterion.<sup>8</sup> Their criterion for the thermochromism was an increase of band B in intensity with raising temperature. The band was not observed for the crystals of **1** and **2** by their absorption spectroscopic measurement on samples of crystalline films even at temperatures just below their melting points, probably because it was too weak in intensity to detect. After extensive examinations of many SAs, they claimed that a given modification of SAs is either photochromic or thermochromic, but not both. The origin of this mutually exclusive character of the chromism is yet to be elucidated. The present study reveals that the chromism of SAs does not have such an exclusive character and that SAs are generally thermochromic in the solid state, whether they are photochromic or not.

In summary, we present here a new perspective on the thermo- and photochromism of salicylideneanilines in the solid state. The study demonstrates that the color of materials can be controlled by a trace of colored species and that the variable-temperature diffuse reflectance spectroscopy is a quite effective tool for its detection, and therefore for the study of chromism in the solid state.

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