

Deuterium isotope effect on the solid-state thermal isomerization of photo-coloured *cis*-keto species of *N*-salicylideneaniline

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Deuterium isotope kinetic effect in the solid state was observed by using thermal fading reaction of photo-coloured species derived from *N*-salicylideneaniline deuteriohydroxyl derivative; thus, the existence of a *cis*-keto form in the photo-coloured Schiff base crystals was suggested experimentally along with 6-methyl-substitution effect on the stability of the photoproduct.

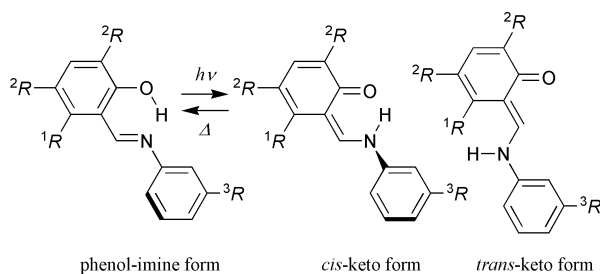
Photo-induced colour change of solid materials has been a subject of increasing interest in materials science due to their potential for various applications.¹ Elucidation of mechanism of the colour change is an important step for the utilization of the phenomenon in photoelectron systems. *N*-Salicylideneaniline (**1**) and its derivatives with some ring substituents are well known to exhibit photo-colouration in the crystal state without any side-reaction.² The colouration process is generally accepted to involve an intramolecular proton transfer from the *o*-hydroxyl group to the imine nitrogen atom followed by framework changes in the molecule.² Recently, Harada, Uekusa, and Ohashi revealed the structure of the photo-coloured species of *N*-(3,5-di-*tert*-butylsalicylidene)-3-nitroaniline (**3**), whose photochrome was extremely stable, to be a *trans*-keto form as a disorder form (occupancy factor = 0.1) by X-ray crystallography (Scheme 1).³ From kinetic studies on the phenomenon, however, more than two photo-coloured species, one of which might be the relatively unstable *cis*-keto form, have been considered for *N*-salicylideneanilines.^{4,5} The crystallography of such a *cis*-keto species, that has a stable shape in the excited state, as a disorder form in the parent enol-imine crystal was difficult because the electron density distribution to the two species was almost impossible due to their close proximity in the crystal. There has been no experimental information for the unstable species in photo-coloured crystals; thus, clarification of the modes of molecular motion in the change process of Schiff bases continues to be of interest in the search for practical utilization of the phenomenon.

The fact that the proton transfer between the hydroxyl group and the imine nitrogen is a key feature in the colour-change of

such a system directed our attention to a deuterium-substitution effect on the proton transfer process of **1**. Although an impressive study by Cohen, Schmidt, and Flavian described that the decay rate of photoproduct of **1** was unaffected by deuteration of the OH group, the thermal decolouration reaction was not analyzed as two consecutive first-order processes in their investigation.⁶ We here report the first successful observation of the deuterium isotope effect on the kinetics of photochromism of *N*-salicylideneaniline in the crystal state to suggest the existence of a *cis*-keto form as a photo-coloured species.

Repeating recrystallization of **1** from methanol-*d*₁ yielded *N*-salicylideneaniline-*d*₁ (**1d**), whose structure was confirmed by the spectral and elemental analytical data.⁷ ¹H NMR peak due to the OH proton (at δ 13.27 ppm in CDCl₃ for **1**) disappeared by the conversion to the OD group in **1d**. IR spectra of **1** and **1d** in hexachlorobutadiene and nujol mulls were almost superimposable except for the characteristic OH stretching band at around 2600 cm⁻¹ for **1** and the broad OD stretching band⁸ at around 2100 cm⁻¹ for **1d**. Since the reflectance spectrum of **1d** was strikingly similar to that of **1**, the electronic state and conformation of both Schiff bases were supposed to be identical in the crystal state.

Photochromic properties of **1** and **1d** were then compared. By irradiating the yellowish crystalline Schiff bases with 365 nm light, the colour was altered to orange and it faded with time in the dark. Reflectance spectra of **1d** before and after UV light irradiation are shown in Fig. 1. Since the electronic spectral changes were the same for both samples, each thermal fading reaction of the photo-coloured species was followed by reflectance spectrophotometry at 30 °C by measuring the optical density at $\lambda = 511$ nm, at which a maximal decrease occurred in the dark. The experimental optical density (*A_t*) vs. time (*t*) data were treated with the standard integrated expression, $kt = \ln\{(A_0 - A_\infty)/(A_t - A_\infty)\}$, for a first-order process using linear least-squares analysis.⁴ The thermal decolouration of the photoproduct went on in two steps. Although the degrees of photo-induced colour change of these crystals and the rate constants of the 2nd step (*k*₂) of the thermal fading of the photoproduct were identical for **1** and **1d**, the rate constants (*k*₁) of the 1st step were different each other (*k*₁ = 1.4 × 10⁻³ s⁻¹ and *k*₂ = 6.0 × 10⁻⁵ s⁻¹ for **1**⁹ and *k*₁ = 7.0 ×



	¹ R	² R	³ R
1:	H	H	H
2:	H	(CH ₃) ₃ C	H
3:	H	(CH ₃) ₃ C	NO ₂
4:	CH ₃	(CH ₃) ₃ C	H

Scheme 1 Photoisomerization of Schiff bases.

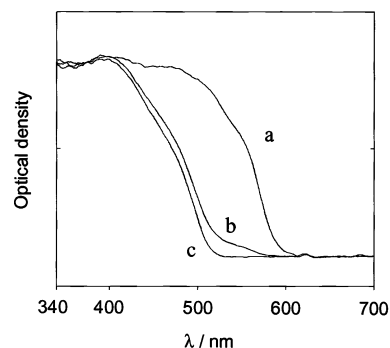


Fig. 1 Reflectance spectra of **1d**: a: Immediately after $\lambda = 365$ nm light irradiation, b: 120 min after irradiation, and c: before irradiation.

10^{-4} s^{-1} and $k_2 = 6.0 \times 10^{-5} \text{ s}^{-1}$ for **1d**, respectively) (Fig. 2). The effect of deuteration of the other hydrogens was investigated; however, no distinct deuterium isotope effect was observed for aromatic ring-deuterated analogue derived from aniline- d_5 and salicylaldehyde.

From these results it is reasonably considered that two consecutive first-order decays of the photo-coloured species are ascribed to the framework relaxation of two types of quinoid-amine form to the original phenol-imine form in the ground state. Thus a *cis*-keto form as well as a *trans*-keto form is assumed to be generated by the photo-irradiation and coexist in the initial photo-coloured crystals to a certain extent. It is easily believed that the thermal back reaction of the *cis*-keto form is much faster than that of the *trans*-keto form, being observed as the initial fading step (rate constant: $k_1' = k_1 - k_2 \approx k_1$), which must be affected by the easiness of intramolecular proton transfer between the amino nitrogen and the quinoid oxygen. The electron density distribution of the quinoid C=C–N–C bond system in the *trans*-keto form, whose thermal rotation is essential to the thermal back reaction to the original phenolic C=C–N–C bond system, is hardly affected by the vibration energy of the N–H(D) group. Thus, the second bleaching step (rate constant: k_2) is attributed to the thermal back reaction of the *trans*-keto form, whose relaxation speed is not influenced by the proton transfer, or some other form in which the N–H–O distance is longer than that in *cis*-keto form. Although the particle size could not be controlled to be uniform, the experimental deviation was small enough for the discussion and the rate constant ratio k_1/k_2 of **1d** was observed to be smaller than that of **1** in every experiment. A *cis*-zwitterionic (NH) form, in which two phenyl rings are in *cis* configuration to each other for the C=N bond, may be proposed as another possible structure of the photoproduct. However, its existence has never been confirmed simply because a necessary reaction room for such isomerization (molecular motion) could not be obtained in the observed crystal lattice of photochromic Schiff bases.

In order to clarify the existence of the *cis*-keto form as the photo-coloured species, we revealed 6-methyl-substitution effect on the stability of the photo-coloured species of Schiff bases. Condensation of aniline and 3,5-di-*tert*-butyl-6-methyl-salicylaldehyde, which was synthesized from 2,4-di-*tert*-butyl-5-methylphenol under standard Reimer–Tiemann conditions,¹⁰ produced Schiff base **4**. The structure of the product was confirmed by the spectral and elemental analytical data.¹¹ By irradiating the yellowish crystalline **4** with 365 nm light, the colour was altered to orange and it faded with time in the dark. The thermal bleaching reaction of the photoproduct was followed by reflectance spectrophotometry at 30 °C to obtain the rate constant, $k = 1.7 \times 10^{-2} \text{ s}^{-1}$. From the inspection of the molecular model and the reported structure of the photo-coloured form of **3**,³ *trans*-keto structure is not possible to be taken for the photoisomer of **4** because of steric hindrance due to the resultant contact of the hydrogen on the nitrogen atom and

the methyl substituent on the phenyl ring. The k value for **4** is assigned to the rate constant of thermal isomerization of photo-coloured *cis*-keto species. In the case of compound **2**, in which such a methyl substituent is absent, the crystals exhibit photochromism and the constructed first-order plots of the photoproduct do not show a single straight line but consist of a two-stage transient decay, demonstrating the existence of two photo-coloured species, *cis*-keto as well as *trans*-keto forms in the crystals ($k_1 = 1.9 \times 10^{-3} \text{ s}^{-1}$ and $k_2 = 1.0 \times 10^{-5} \text{ s}^{-1}$).⁴ The quantitative difference of the rate constants of k for **4** and k_1 for **2** is ascribed to the steric repulsion of the methyl substituent in **4**, for which formation of a planar *ortho*-quinoid form is disturbed in part.

From the kinetic measurements for the thermal fading reaction of the photo-coloured species derived from *N*-salicylideneaniline, its deuteriohydroxyl derivative, and *N*-(6-methylsalicylidene)aniline derivative, the initial stage of two consecutive processes was ascribed mainly to the molecular framework relaxation concerned with the intramolecular proton transfer in a *cis*-keto form existing in the photo-coloured Schiff bases. The deuterium isotope effect on the solid state reaction rate k_H'/k_D' was calculated to be 2.1. The reason for the small isotope effect on the rate constant may be responsible for the characteristics of solid state isomerization, which is faintly affected by the vibration energy of the N–H(D) group.¹² Such an *O*-deuterium isotope effect at the former step of the thermal decolouration of the photo-coloured species of Schiff base was observed in some *N*-salicylidenebenzylamine crystals in this laboratory. It was found that the kinetic isotope effect was small in the solid state but still effective to reveal isomerization reaction mechanisms.

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- 4**: Yellow fibers; mp 104–111 °C (Found: C, 81.62; H, 9.14; N, 4.19. $\text{C}_{22}\text{H}_{29}\text{NO}$ requires C, 81.69; H, 9.04; N, 4.33%); δ_{H} (270 MHz; CDCl_3): 1.44, 1.46 (9H, s, $(\text{CH}_3)_3\text{C}$), 2.67 (3H, s, CH_3), 7.25–7.48 (6H, m, 2(H), 3(H), 4(H), 5(H), 6(H), 4'(H)), 9.12 (1H, s, CH=N), 14.79 (1H, s, OH). IR (KBr): 2955, 1610, 1578, 1468, 1436, 1388, 1295, 1242, 1192, 1157, 845, 760, 689 cm^{-1} .
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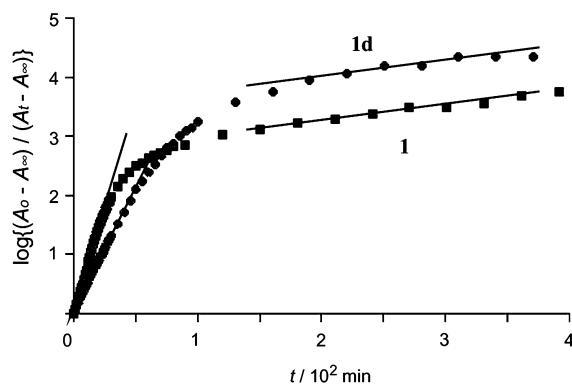


Fig. 2 Kinetic plots of optical density decrease for the photochromes derived from **1** and **1d**. The solid lines show the least-squares linear regression slopes.