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Spectroscopic and Kinetic Studies of the Photochromism of *N*-Salicylideneanilines and Related Compounds

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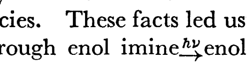
Photochromism of *N*-salicylideneanilines and related compounds was studied by measuring the electronic and vibrational spectra of the transient species. The rise time of the transient electronic spectra of the photochromic colored species was measured by picosecond time-resolved spectroscopy and was found to be dependent upon solvent viscosity. FT IR spectra showed that the photochromic colored species took the keto amine form. Picosecond kinetic analysis demonstrated that an intermediate existed in the transfer process from *cis*-keto amine to the photochromic species. These facts led us to the conclusion that the photochromic phenomenon of *N*-salicylideneanilines occurred through enol imine$\xrightarrow{h\nu}$enol imine*→*cis*-keto amine*→the intermediate→*trans*-keto amine(photochromic species).

A number of *N*-salicylideneanilines have been reported to be photochromic both in crystal and in rigid and fluid solutions.1—5) Cohen and his co-workers showed that the hydroxyl group is essential for the photochromic effect: The effect vanishes when the *o*-hydroxyl group is methylated or the Schiff's bases are derived from benzaldehyde or *p*-hydroxybenzaldehyde.2a)

Several studies have indicated that photochromic change occurs through hydrogen transfer followed by a geometrical rearrangement of the molecule.1a,2a,3b,4a,5) Ottolenghi and his co-workers first proposed that the rearrangement is the cis-trans isomerization due to rotation about the C_1–C_7 bond,5b) and later proposed mainly on the basis of theoretical consideration that the rotation takes place both about the C_1–C_7 bond and about the C_7–N bond, resulting in two non-planar photochromic colored species.5c)



In the present investigation we attempted to elucidate the primary process of photochromism of *N*-salicylideneanilines and related compounds by using the time-resolved spectroscopy techniques in the time range of millisecond to picosecond and to clarify the molecular structure of the photochromic colored species by means of FT(Fourier transform) IR spectroscopy.

Experimental

The compounds employed in the present work are *N*-salicylidene-*p*-toluidine (**1**), *N*-salicylidene-*o*-toluidine (**2**), 2-chloro-*N*-salicylideneaniline (**3**), *N*-salicylidene-*m*-toluidine (**4**), *N*-salicylidene-*m*-toluidine[hydroxy-*d*] (**5**), *N*-3-methoxysalicylidene-4-nitroaniline (**6**), *N*-[1-(*o*-hydroxyphenyl)ethylidene]-aniline (**7**), *N,N'*-disalicylideneethylenediamine (**8**), and 2-(*o*-hydroxyphenyl)benzothiazole (**9**).

Compounds **1**—**4** and **6**—**8** were synthesized by direct condensation of the appropriate carbonyl compounds with corresponding amines in ethanol, and were purified by recrystallization and vacuum sublimation. **5** was prepared by treating **4** in excess CH_3OD for 8 h, the isotopic purity being determined to be about 90% by means of NMR spectroscopy. Commercially available **9** was chromatographed from benzene on activated alumina. Spectrograde diethyl ether, methylcyclohexane, and toluene, GR grade cyclohexanol and liquid paraffin were used without further purification. The other solvents used were purified according to the usual method.6)

A flash photolysis apparatus constructed by Kira and Nishi7) was used for measurements of time-resolved absorption spectra in the time range longer than microsecond. A Blumlein type N_2 laser with a pulse-width of 3.6 ns (FWHM) and with a peak power of 500 kW was constructed to be used as an exciting light source for photolysis in the nanosecond time range and for determination of the fluorescence decay time. For the nanosecond time-resolved spectroscopy, a pulsed Xe flash with about 3 μs half-duration was used as an analyzing light source. The light intensity was detected with an HTV 1P28 photomultiplier through a 0.25 m Jarrel-Ash grating monochromator (JE 25). A TRW Model 32A decay time computer was used for determination of the fluorescence lifetime.

An amplified single pulse selected from a pulse train of a mode-locked ruby laser (JEOL JLS-R10) was used for the picosecond time-resolved spectroscopy experiment. The pulse width was *ca.* 20 ps. The exciting light pulse at 347.2 nm was obtained by the frequency-doubling of 694.3 nm fundamental through an ADP crystal. Details of the apparatus were published elsewhere.8)

FT IR spectra were measured with a JEOL FT IR spectrophotometer JIR-03F at the Department of Chemistry, The University of Tokyo.

Results and Discussion

Photochromic Colored Species of N-*Salicylideneanilines.* Transient absorption spectra of **1**—**3** and **7**—**9** were measured in PM (a mixed solvent of isopentane and methylcyclohexane with 1:1 volume ratio) at room temperature. Photochromic effect was examined for **4** and **5** in crystalline state. Since **6** is scarcely soluble in PM, the mixed solvent of diethyl ether and toluene (1:1 volume ratio) was used for the measurement of the transient absorption spectrum of **6**. Some of the transient absorption spectra are shown in Figs. 1 and 2. The observed spectra and their decay kinetics are not affected by dissolved O_2. This result is consistent with the previous result.3) The fact that compounds **1**—**9** commonly having the enol imine structure show the photochromic effect leads us to the conclusion that the structure is essential to formation of the photochromic species.

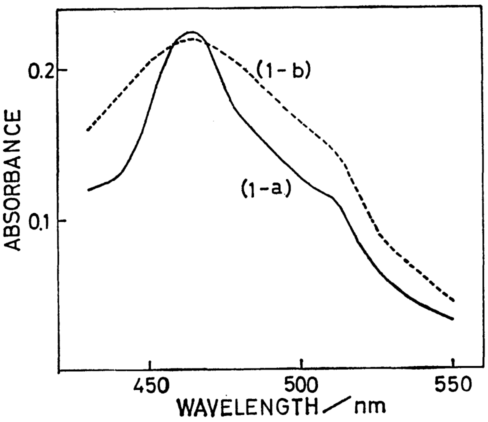


Fig. 1. The photochromic transient absorption spectrum of **1** in PM at 293 K: 1-a, 10 ns after triggering (the 1.4×10^{-3} M solution, 10 mm cell length); 1-b, 35 μs after triggering (the 1.4×10^{-4} M solution, 100 mm cell length).

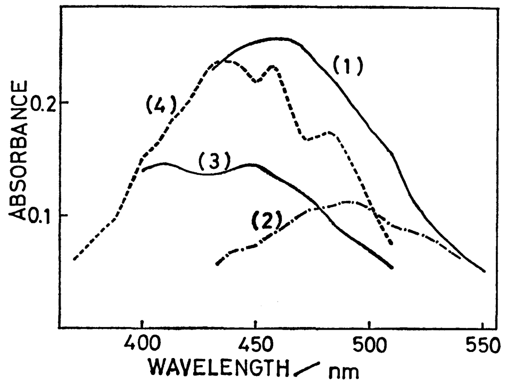


Fig. 2. The photochromic transient absorption spectra of **3**, **6**, **7**, and **8** at 293 K: (1), **3** in PM, 35 μs after triggering (1.7×10^{-4} M); (2), **6** in diethyl ether–toluene (1: 1), 90 μs after triggering (8.4×10^{-5} M); (3), **7** in PM (1.0×10^{-3} M), 10 ns after triggering; (4), **8** in PM (1.8×10^{-4} M), 35 μs after triggering.

Fading of the photochromic colored species of **3** and **6** follows first-order kinetics within the limitations of experimental error, and their decay times were derived to be 55 and 440 μs, respectively, while that of **1**, **2**, **8**, and **9** follows neither first-order nor second-order kinetics. Kinetic analysis at every 10 nm in the measured wavelength region for **1**, **2**, **8**, and **9** shows that there are two different kinds of contributions to the fading: a large but narrowly-distributed contribution from the short-lived component and a small but widely-distributed contribution from the long-lived component. This can explain the observation that the transient absorption bands of **1** becomes blurred with increasing time.

The decay curves observed with **1**, **2**, **8**, and **9** were analyzed by resolving into the long- and short-lived components. The results are given in Table 1 together with those for **3** and **6**. We can see that the decay time of the photochromic colored species is dependent on the solvent viscosity. This is important in connection with the mechanism of the photochromic phenomenon.

The Structure of the Photochromic Colored Species. On the basis of indirect evidence there have been several proposals that the photochromic colored species is formed by hydrogen transfer in the excited state followed by a molecular rearrangement.[1–5] We obtained for the first time the direct evidence that the photochromic colored species take the keto amine form in the crystalline state. IR difference spectra recording transmittance ratios ($T=I_1/I_2$) *vs.* wave numbers were measured with **4** and **5** in KBr disk at room temperature. Here I_1 and I_2 represent transmitted light intensity before and after irradiation with UV light (Hg 365 nm line), respectively. Crystal of **4** was taken as a sample since it gave a long-lived photochromic colored species at room temperature. For the convenience of assignment of the vibrational bands deuterated anil **5** was examined at the same time. The result of **4** is shown in Fig. 3. The frequencies of the characteristic bands observed with **4** and **5** are given in Table 2. Bands with $T>1$ and $T<1$ are attributed to the parent compounds (**4** and **5**) and the photochromic colored species, respectively.

From the characteristic bands with $T>1$ such as C=N stretching at 1616 cm^{-1}, the skeletal streching of a benzene ring at 1597 and 1570 cm^{-1}, and the OH out-of-plane angle bending at 837 cm^{-1}, we can see that the parent compounds **4** and **5** take the enol imine form in the crystalline state. This is consistent with the

Table 1. Decay times of the photochromic colored species

No.				
3	55 μs (in PM)			
6	440 μs (in diethyl ether–toluene)			
	S	L	S	L
	in PM		in LP	
1	30±10 μs	70±20 μs	0.9±0.3 ms	3±1 ms
2	30±10 μs	70±20 μs		
8	30±10 μs	130±30 μs		
9	30±10 μs	80±30 μs	2±1 ms	7±2 ms

S: Short-lived component, L: Long-lived component, LP: Liquid paraffin.

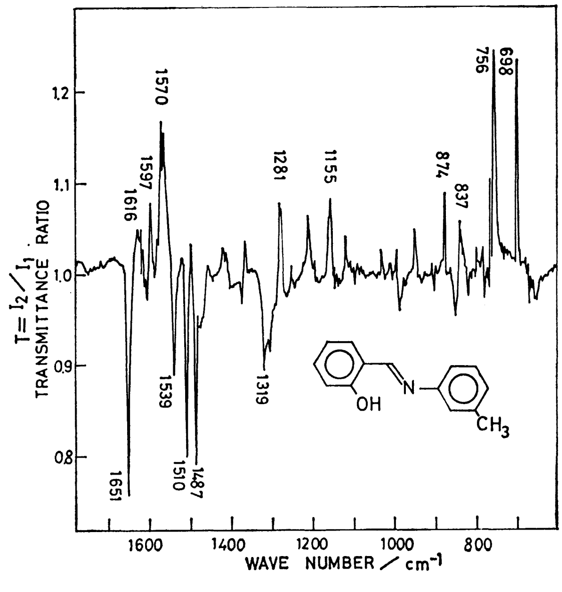


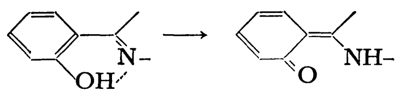
Fig. 3. IR difference spectrum of the photochromic colored species of **4** in KBr disk at 298 K.

Table 2. Characteristic IR bands of the enol imine and keto amine forms of *N*-salicylideneanilines

	Vibrations	**4**	**5**
$T>1$	$\nu_{C=N}$	1616	1620
	Ring skeletal stretching	1597 1570	1597 1570
	γ_{OH}	837	
	γ_{OD}		613
	$\gamma_{CH}{}^{a)}$	756	756
$T<1$	$\nu_{C=O}$	1651	1644
	Amide vinylog and ring skeletal stretching	1539 1510 1487	1529 1505 1487
	ν_{C-N}	1319	1319

All frequencies are given in cm^{-1}. (KBr disk at 298 K.) a) *o*-Disubstituted benzenes.

results obtained by X-ray crystal analysis.[9] Concerning the bands with $T<1$, strong absorption bands at 1651 cm^{-1} for **4** and 1644 cm^{-1} for **5** show that the photochromic colored species has the carbonyl group. Furthermore, the species show the skeletal stretching of a quinoid ring and the amide vinylog NHC=CC=O vibration at 1539, 1510, and 1487 cm^{-1}, and the C–N stretching at 1319 cm^{-1} for **4**. These results clearly demonstrate that the photochromism is caused by photoisomerization of the enol imine to the keto amine:



enol imine keto amine

Photochromic Schiff's bases are known to exhibit similar transient electronic absorption spectra in crystalline state and in rigid and fluid solutions.[1–5,10] This means that the photochromic colored species has the same structure, the keto amine form, both in crystalline phase and in rigid and fluid solutions.

Picosecond Photolysis and the Mechanism of Photochromism. We determined for the first time the rise times of the photochromic transient absorption for **1** and **9**, and clarified the existence of the precursor of the photochromic colored species by using the picosecond time-resolved spectroscopy technique. In the PM solution of **1** with viscosity of 0.40 cP at 25 °C, absorbance at 465 nm was saturated 200 ps after photoexcitation and the rise time was determined to be 84 ps (Fig. 4-A). On the other hand, in the cyclohexanol solution with viscosity of 47 cP at 27 °C, the absorbance of **1** at 475 nm continued to increase 200 ps after photoexcitation and its rise time was estimated to be longer than 180 ps (Fig. 4-B). This means that the enol imine in the excited singlet state passes over an energy barrier sensitive to viscosity in the course of transformation into the photochromic colored species; in other words, that in the photochromic phenomenon the hydrogen transfer in the excited state is followed by a geometrical change in the molecular framework which is sensitive to viscosity. The occurrence of the geometrical change in the photochromic process is also supported by the fact that the electronic absorption spectrum of the photochromic colored species is different from that of the *cis*-keto amine formed simply by the hydrogen transfer in the ground state.[5c)]

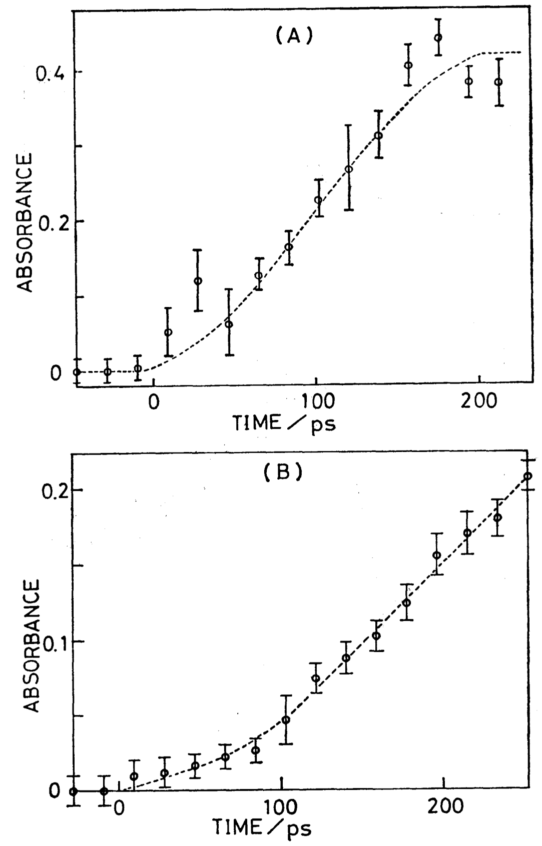
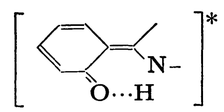
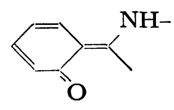


Fig. 4. Formation of the photochromic colored species of **1**. (A) Absorbance at 460 nm plotted as a function of time at 298 K (1.1×10^{-3} M in PM). (B) Absorbance at 475 nm plotted as a function of time at 300 K (1.7×10^{-3} M in cyclohexanol).

Since the keto amine can take *cis*- and *trans*-forms, it is reasonable to consider that the photochromic colored species is the *trans*-keto amine, and that the photochromic process involves the transformation of the *cis*-keto amine in the excited state into the *trans*-keto amine in the ground state.



cis-keto amine in the excited state



trans-keto amine

According to this mechanism, the thermal bleaching of the photochromic colored species is conversion of the *trans*-keto amine to the enol imine and involves the rearrangement of the molecular framework besides the intramolecular hydrogen transfer. This scheme for the thermal bleaching gives a reasonable explanation to the following findings:

(1) The half-life of the photochromic colored species of **4** in crystalline phase is 1300 and 200 min at 16 and 27 °C, respectively.[11)]

(2) The fading kinetics of the photochromic colored species in fluid solution is dependent on viscosity of the solvent.

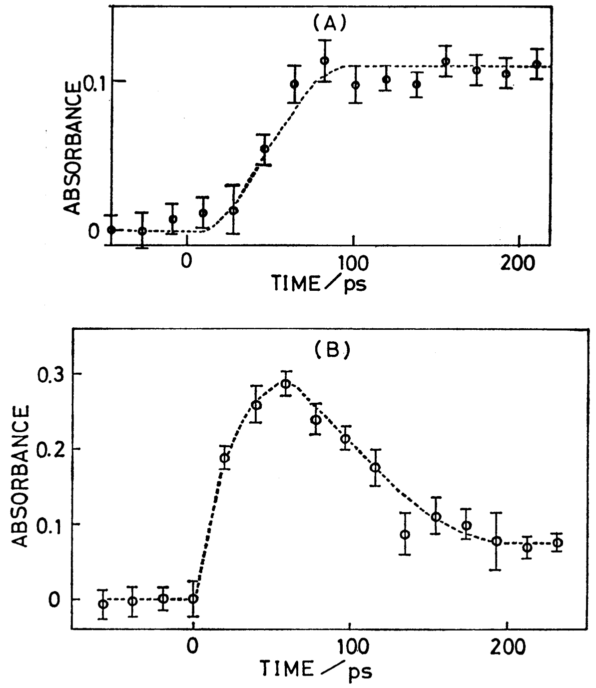


Fig. 5. (A) Formation of the photochromic colored species of **9** at 293 K (1.3×10^{-3} M in PM). Absorbance at 470 nm plotted as a function of time. (B) Decay of the intermediate X* of **9** at 293 K (8.8×10^{-4} M in PM).

The rise time of the photochromic colored species was measured with **9** in PM at 20 °C to be 56 ps (Fig. 5-A). In addition, the transient absorption with very short lifetime was observed with **9** in PM at 20 °C. Absorbance at 385 nm was plotted as a function of time in Fig. 5-B. There are two kinds of contributions to absorbance at 385 nm; the short-lived and the long-lived components. The decay time of the short-lived component was determined to be 53 ps[12)] in agreement with the rise time of the long-lived component (the photochromic colored species). Therefore, the short-lived component is considered to be the precursor of the photochromic colored species. On the other hand, the decay time of the fluorescent state of the *cis*-keto amine was determined to be 0.7 ns. These observations clearly show that the molecular rearrangement of the *cis*-keto amine to the photochromic colored species does not occur from the fluorescent state, but originates from the precursor with the lifetime of 53 ps, which may be considered to be the higher vibrationally excited state of the *cis*-keto amine. Rosenfeld *et al.* derived a similar conclusion for *N*-salicylideneaniline from the exciting wavelength dependence of the quantum yields of the photochromic colored species and the fluorescence of the *cis*-keto amine.[5c)] We have concluded directly and definitely the existence of the precursor.

A scheme for formation of the photochromic colored species by photoexcitation of the enol imine in the ground state, E, is represented in Fig. 6. The excited singlet state E* of the enol imine produced by photoexcitation of E results in formation of the photochromic colored species in the ground state, P, through the hydrogen transfer and the molecular rearrangement (cis-trans isomerization). The intermediate X* is an excited singlet state from which the photochromic colored species and the fluorescent state of the *cis*-keto amine, K_f*, originate.

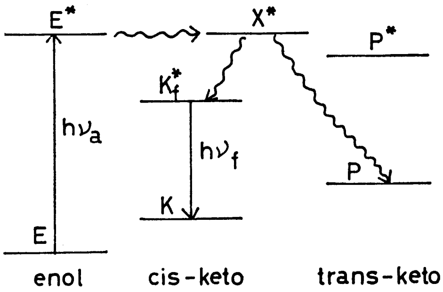


Fig. 6. Schematic explanation of the photochromic species formation.

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[12)] We defined the following quantities:
$A(t)$ = absorbance t ps after photoexcitation,
$A(\infty)$ = the final value of absorbance,
$D(t)=A(t)-A(\infty)$.
From the plot of log $D(t)$ *vs.* time, t, the decay time of the short-lived component was determined to be 53 ps.