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Elongated Lifetime of Unstable Colored Species by Intermolecular Hydrogen Bond Formation in Photochromic Crystals

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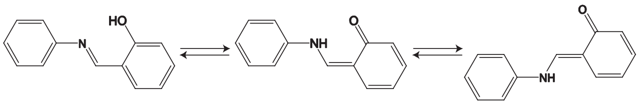
The crystallization of *N*-3,5-di-*tert*-butylsalicylidene-3-carboxyaniline (**1**) from a methanol solution gave three crystal forms, **1α**, **1β**, and **1γ**. The colorless **1α** and pale yellow **1β** turned red when they were irradiated with UV light whereas orange **1γ** showed no color change. The lifetimes of the colored crystals were estimated to be 17 and 780 min at room temperature for **1α** and **1β**, respectively, from IR spectra. The structure of the colored **1α** crystal was analyzed by X-ray at 93 K. In addition to the original enol form of **1**, the *trans*-keto form appeared on the difference electron density map with an occupancy factor of 0.117(2). This indicates that the color change was caused by the structural change from the enol to *trans*-keto form, which is the same as the color change previously reported in the crystal of *N*-3,5-di-*tert*-butylsalicylidene-3-nitroaniline (**2**) (lifetime, 1200 min). It was made clear from the structures of the *trans*-keto forms in the crystals of **1α**, **1β**, and **2** that the lifetime of the unstable colored form should be determined by the possibility and the strength of the intermolecular hydrogen bond formation of the N–H group of the *trans*-keto form to the neighboring molecules.

Light-induced reversible color change of substances is known as photochromism and organic photochromic compounds have attracted much attention over the past decades for their applications in optic data storage, electronic display systems, optical switching devices, ophthalmic glasses, and so on.[1] *N*-Salicylideneanilines, which are the condensation products of salicylaldehydes and anilines, exhibit photochromism both in solution and in the solid state.[2] Photochromic salicylideneanilines are usually pale yellow and exist in the enol form in crystals. It was proposed from spectroscopic data that the hydrogen atom of the hydroxy group is translocated to the imine nitrogen atom on irradiation with ultraviolet light. A subsequent geometrical rearrangement in the excited state is assumed to form a red photoproduct. The deep red color can be erased by irradiation with visible light or by thermal fading in the dark. Although many studies have been carried out over three decades, there remains a controversy about the structure of the colored species.[3] In a previous paper, we analyzed directly the structure of the photoinduced colored species of *N*-3,5-di-*tert*-butylsalicylidene-3-nitroaniline (**2**) by X-ray using two-photon excitation, which was the first crystallographic determination of structural change showing reversible photochromism in organic crystals.[4] This crystal was selected because the photoproduct has the longest lifetime among a variety of salicylideneaniline crystals.[5] The molecular structure before irradiation takes the enol form. The pale yellow crystal turned dark red when it was irradiated with laser light of 730 nm, twice the wavelength of the absorption maximum at 365 nm at room temperature. After the laser irradiation, the crystal structure was determined by X-ray diffraction analysis. The difference electron density map showed additional peaks around the original enol form. The peaks clearly indicated that the new product with *trans*-keto form was produced in the red form crystal. It is clear that the color change is caused by the transformation from the enol to *trans*-keto form through the *cis*-keto form as shown in Scheme 1.

After our work, Fukuda et al. reported the structures and photochromic properties of *N*-(3,5-dihalosalicylidene)-2,6-dialkylaniline derivatives. They found that some crystals showed no photochromism although the two phenyl rings of the molecules are not co-planar and the dihedral angles become more than 60° due to the steric repulsion between the azomethine hydrogen atom and the alkyl groups at the 2,6-



enol cis-keto trans-keto

Scheme 1. Reaction mechanism of the photochromism of *N*-salicylideneaniline, including the hydrogen transfer and pedal motion.

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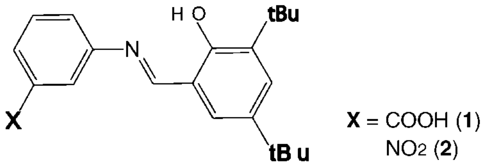


Scheme 2. Structures of *N*-salicylideneaniline derivatives **1** and **2**.

positions of the aniline ring. They proposed that the crystal packing should play an important role in the photochromic properties.[6] Amimoto and Kawato also wrote a review article of photochromism of organic compounds in the crystalline state.[7] Fujiwara et al. made clear from variable-temperature diffuse reflectance spectroscopy that the enol form of salicylideneanilines is inherently colorless but that the pale yellow observed usually should be due to a trace of the *cis*-keto form which is in equilibrium thermally with the enol form at room temperature. The photo transformation from the *cis*-keto to *trans*-keto form was also found. They proposed that the salicylideneanilines are generally thermochromic in the solid state whether they are photochromic or not. They also proposed the direct change from enol to *trans*-keto form from the spectral change, although the structural confirmation was obscure.[8] Harada et al. reported the fluorescence spectra in the solid-state thermochromism of salicylidene aniline.[9]

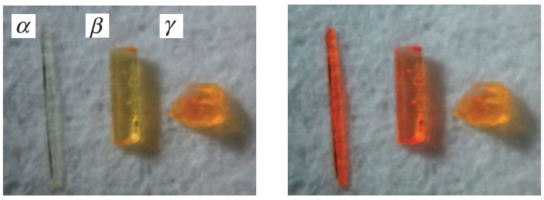
The above results clearly show why photochromism occurs in the crystal. However, it remains unclear why the unstable colored species of different crystals have different lifetime in photochromism. Recently Mikami and Nakamura proposed from theoretical calculations based on the structure of the *trans*-keto form produced in photo colored crystal[4] that the long lifetime of the colored species of **2** is due to the intermolecular hydrogen bond, which is formed between the photo-produced *trans*-keto form and the nitro group of the neighboring molecule.[10] However, no experimental support has been observed yet.

Recently we found that three polymorphs, **1α**, **1β**, and **1γ**, were formed in the crystallization of *N*-3,5-di-*tert*-butylsalicylidene-3-carboxyaniline (**1**) (Scheme 2). When the crystals were irradiated with UV light, **1α** and **1β** showed photochromism whereas **1γ** was unchanged. Moreover, the lifetimes of the colored species of **1α** and **1β** forms were quite different. The present paper reports the origin of the different lifetime of the colored species of salicylideneanilines based on X-ray crystal structure analysis.

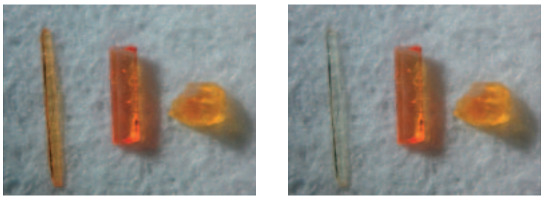
Experimental

Preparation. Compound **1** was prepared by direct condensation of 3,5-di-*tert*-butylsalicylaldehyde with 3-carboxyaniline (*m*-benzoic acid) in methanol. The three different forms, **1α** (colorless needle), **1β** (pale yellow parallelepiped), and **1γ** (orange block), were obtained in the same batch of methanol solution, which are shown in Figure 1a.

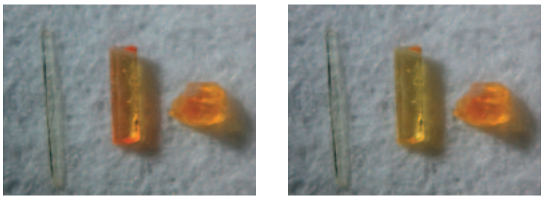
Identification of Photochromism. A powdered sample of each form (7 mg) was mixed with powdered $MgSO_4$ (350 mg) and then the mixed sample was irradiated with a high-pressure mercury lamp (SAN-EI UVF-352S) at room temperature through a glass-filter (HOYA UV360) which transmits light with wavelengths around 360 nm. The UV–visible spectra were measured with a JASCO V-560 spectrometer equipped the option (ISV-469) for diffuse reflectance spectroscopy.



(a) Before irradiation (b) After irradiation



(c) 30 min (d) 60 min



(e) 80 min (f) 72 h

Figure 1. Color changes of **1α**, **1β**, and **1γ**: (a) before irradiation, (b) after UV irradiation for 10 h, (c), (d), (e), and (f) after 30, 60, 80 min, and 72 h, respectively, kept in the dark after UV irradiation.

Observation of Thermal Fading. Sufficient crystal was selected for each form and was irradiated with the high-pressure mercury lamp through the glass-filter more than 10 h at room temperature. The red colors observed in **1α** and **1β** form gradually faded, which were observed by microscope as shown in Figure 1.

Measurement of Lifetime. KBr pellets (0.5 wt %) of the **1α**, **1β**, **1γ**, and **2** were prepared and were irradiated with the high-pressure mercury lamp through the glass-filter. The FTIR spectra of each pellet were recorded with an Excalibur FTS 3000 instrument (Bio-Rad). A new absorption band appeared around 3400 cm^{-1}, which was assigned to the N–H stretching vibration mode of the produced *trans*-keto form. After the band intensity was completely saturated, the irradiation was stopped and the band intensity was recorded at room temperature in an appropriate time interval. The band intensity gradually decreased. The rate constant, k, and lifetime, τ, were calculated, assuming the first-order kinetics as follows; $kt = \ln(I_0/I_t)$, where I_0 and I_t are the intensities of the N–H frequencies at 0 and t min, respectively, and $\tau = 1/k$.

Crystal Structure Analyses of 1α, 1β, and 1γ before Irradiation. The intensity data were collected at room temperature on a Bruker SMART-CCD diffractometer for **1α** and **1γ** and on a Rigaku R-AXIS RAPID for **1β**. Graphite-monochromatized Mo Kα radiation was used with the Rigaku rotating-anode generator (50 kV, 250 mA). Each structure was solved by the direct method with the program SHELXS-97[11] and was refined by the full-matrix least-squares method with SHELXL-97.[12] All the non-hydrogen atoms were refined with anisotropic temperature factors. The hydrogen atoms of the enol and imine groups were located on the difference electron density map and the other

Table 1. Crystal Data and Experimental Details of the Three Polymorphs before Irradiation

	$\mathbf{1\alpha}$	$\mathbf{1\beta}$	$\mathbf{1\gamma}$
Chemical formula	$C_{22}H_{27}NO_3$	$C_{22}H_{27}NO_3$	$C_{22}H_{27}NO_3$
Formula weight	353.45	353.45	353.45
Temperature/K	295(2)	293(2)	295(2)
Wavelength/Å	0.71073	1.54178	0.71073
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	$C2/c$
a/Å	14.8270(4)	17.5397(5)	16.8640(3)
b/Å	6.0470(2)	6.4058(2)	24.5308(3)
c/Å	22.1811(6)	18.9509(5)	9.74400(10)
β/°	91.1540(10)	107.3700(10)	94.3100(10)
Volume/Å^3	1989.33(10)	2043.69(10)	4019.57(10)
Z	4	4	8
Calculated density/Mg m^{-3}	1.181	1.149	1.168
$F(000)$	760	760	1520
Crystal size/mm^3	0.3 × 0.10 × 0.10	0.15 × 0.15 × 0.15	0.40 × 0.30 × 0.26
θ range/°	1.64 to 27.50	2.62 to 68.23	1.47 to 27.50
Limiting indices	$-19 \le h \le 19$	$-21 \le h \le 20$	$-21 \le h \le 21$
	$-7 \le k \le 7$	$-7 \le k \le 7$	$-31 \le k \le 31$
	$-28 \le l \le 28$	$-21 \le l \le 20$	$-21 \le l \le 21$
Reflections collected/unique	25756/4561	23707/3697	27159/4634
R(int)	0.0628	0.0323	0.0644
Completeness to θ/%	100	98.6	100
Refinement on	Full-matrix least-squares on F^2		
Data/restraints/parameters	4561/0/250	3697/0/248	4634/0/288
Goodness-of-fit on F^2	1.033	1.096	0.995
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0436$	$R_1 = 0.0454$	$R_1 = 0.0483$
	$wR_2 = 0.1093$	$wR_2 = 0.1267$	$wR_2 = 0.1544$
Extinction coefficient	0.0165(18)	0.0025(3)	0.0035(6)
Largest diff. peak and hole/e Å^{-3}	0.240 and −0.157	0.209 and −0.147	0.237 and −0.222

hydrogen atoms were obtained geometrically. The crystal data and the experimental details are listed in Table 1.

Crystal Structure of 1α after Photoirradiation. Since it was very difficult to apply the two-photon excitation technique because of its short lifetime, a very thin crystal of 0.35 × 0.15 × 0.03 mm^3 was selected. The intensity data were collected at 93 K on the SMART-CCD diffractometer. Then the crystal was irradiated with UV light on the diffractometer using the high-pressure mercury lamp through the glass filter at 267 K not to return to the original colorless crystal. After 40 min the irradiation was stopped and the crystal was cooled to 93 K and the intensity data were collected under the same conditions as those before irradiation. On the difference electron density map there appeared new peaks, which were assigned to the *trans*-keto form. In the final refinement, the chemical restraints were applied to the *trans*-keto form. The occupancy factor of the *trans*-keto form became 0.117(2). Then the crystal was irradiated with a xenon lamp (SAN-EI SUPER BRIGHT 152S with USHIO xenon short-arc lamp UXL-151DO) at 265 K. The crystal color changed from red to colorless. The intensity data were collected under the same conditions at 110 K. The analyzed structure is essentially the same as that before irradiation. There are no residual peaks due to the *trans*-keto form in the difference electron density map. This indicates that the *trans*-keto form completely returned to the original enol form on exposure to the visible light. The crystal data of **1α** at the three stages, before and after irradiation with the mercury lamp and after irradiation with the xenon lamp, are listed in Table 2.

Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition numbers CCDC-695393, -695394, -695395, -695396, -695397, and -695398 for **1α**, **1β**, **1γ**, **1α** before UV irradiation, **1α** after UV irradiation, and **1α** after Xe irradiation, respectively. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (of from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Results and Discussion

Crystal and Molecular Structures of the Three Forms. The crystal structures of **1α**, **1β**, and **1γ** before irradiation at room temperature are shown in Figures 2, 3, and 4, respectively. Although there is only one molecule in an asymmetric unit in each crystal, the crystal structures are completely different from one another. The 3-carboxyl group in each crystal makes hydrogen bonds with the neighboring one to form a dimer structure. The O–H···O distances and the O–H···O angles of the three crystals are listed in Table 3.

The molecular structures in **1α**, **1β**, and **1γ** are shown in Figure 5. The selected bond distances and angles and torsion angles are also listed in Table 4. The corresponding values except the torsion angle are in good agreement with one another. The torsion angle of the aniline ring in **1α** is different from the other two. The 3-carboxyl group of the aniline ring in **1α** takes an opposite position to the 2-hydroxy group of the salicylaldehyde ring, whereas the 3-carboxyl groups in **1β** and **1γ** occupy the same side. Moreover, the conformation of the 3-carboxyl group in **1β** to the phenyl ring is opposite to that of

Table 2. Crystal Data and Experimental Details of **1α** before and after UV Irradiation and after Xe Irradiation

	Before UV irradiation	After UV irradiation	After Xe irradiation
Chemical formula	$C_{22}H_{27}NO_3$	$C_{22}H_{27}NO_3$	$C_{22}H_{27}NO_3$
Formula weight	353.45	353.45	353.45
Temperature/K	93(2)	93(2)	110(2)
Wavelength/Å	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a/Å	14.8002(4)	14.8614(4)	14.7988(3)
b/Å	5.9940(2)	5.9932(2)	5.9983(2)
c/Å	21.82130(6)	21.8552(6)	21.8634(5)
β/°	91.331(2)	91.606(2)	91.2430(10)
Volume/Å^3	1935.30(8)	1945.82(10)	1940.31(9)
Z	4	4	4
Calculated density/Mg m^{-3}	1.213	1.207	1.210
F(000)	760	760	760
Crystal size/mm^3	0.35 × 0.15 × 0.03	0.35 × 0.15 × 0.03	0.35 × 0.15 × 0.03
θ range/°	1.64 to 25.00	1.64 to 25.00	1.64 to 25.00
Limiting indices	$-17 \leq h \leq 17$ $-7 \leq k \leq 7$ $-25 \leq l \leq 25$	$-17 \leq h \leq 17$ $-7 \leq k \leq 7$ $-25 \leq l \leq 25$	$-17 \leq h \leq 17$ $-7 \leq k \leq 7$ $-25 \leq l \leq 25$
Reflections collected/unique	20266/3398	20453/3697	27159/4634
R(int)	0.0343	0.0444	0.0335
Completeness to θ/%	99.9	99.9	99.9
Refinement on	Full-matrix least-squares on F^2		
Data/restraints/parameters	3398/0/250	3415/5/239	3404/0/250
Goodness-of-fit on F^2	1.039	1.082	1.051
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0344$ $wR_2 = 0.0877$	$R_1 = 0.0442$ $wR_2 = 0.1029$	$R_1 = 0.0342$ $wR_2 = 0.0877$
R indices (all data)	$R_1 = 0.0402$ $wR_2 = 0.0913$	$R_1 = 0.0528$ $wR_2 = 0.1066$	$R_1 = 0.0408$ $wR_2 = 0.0911$
Extinction coefficient	—	0.0155(14)	—
Largest diff. peak and hole/e Å^{-3}	0.163 and −0.236	0.270 and −0.292	0.177 and −0.192

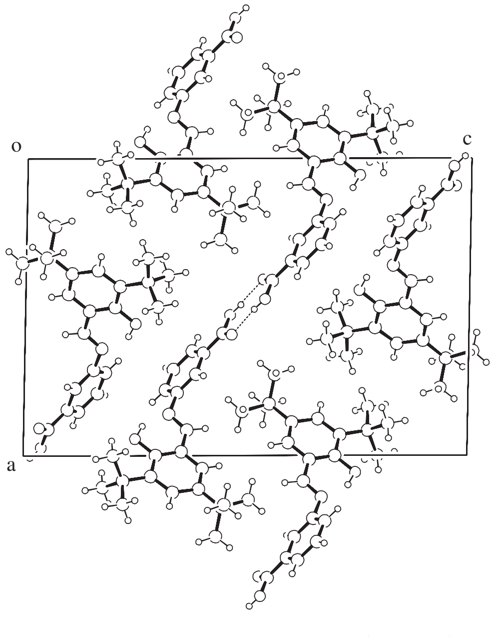


Figure 2. Crystal structure of **1α** viewed along the b axis.

1γ. Such different torsion angles of the 3-carboxyl groups in the three forms are caused by the different intermolecular hydrogen bonds. The torsion angles of the salicylidene moieties are in fair agreement with one another.

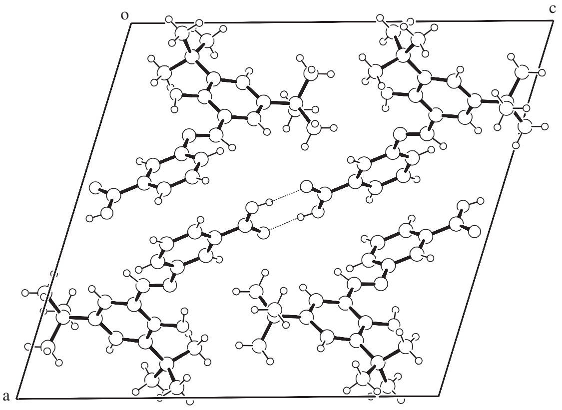


Figure 3. Crystal structure of **1β** viewed along the b axis.

Photochromic Properties. The color changes of **1α**, **1β**, and **1γ** forms during the UV irradiation are shown in Figure 1. Before irradiation, the colors of **1α**, **1β**, and **1γ** are colorless, pale yellow, and orange, respectively. The crystal of **1α** and **1β** turned red and converged after 40 min photoirradiation whereas **1γ** was unchanged. The UV–visible spectra of the three forms before and after 40 min irradiation are shown in Figure 6. The crystal of **1α** showed no absorption at wavelengths more than

450 nm before irradiation but a new absorption band appeared between 420 and 600 nm. The color change from colorless to red corresponds to the new band. The absorption band of **1*β*** before irradiation has a tail to wavelength longer than 450 nm. This causes the pale yellow color of **1*β*** before irradiation at room temperature. After the irradiation, a similar band to that of **1*α*** appeared between 420 and 600 nm. This corresponds to the color change of **1*β*** from pale yellow to red. On the other hand, **1*γ*** showed no new absorption after photoirradiation, so color change was not observed. An absorption tail was also observed from 450 to 550 nm before and after irradiation. This causes the orange color of **1*γ***. The absorption tails observed in **1*β*** and **1*γ*** may indicate that not only the major portion of the enol form but also the minor portion of the *cis*-keto form co-exists in the crystal as suggested by Fujiwara et al.[8]

The red color appearing in **1*α*** and **1*β*** gradually faded when the crystals were kept in the dark at room temperature. The color of **1*α*** returned to the original after 60 min, whereas only a slight change was observed for **1*β*** after 60 min. After 72 h, **1*β*** showed the original pale yellow color.

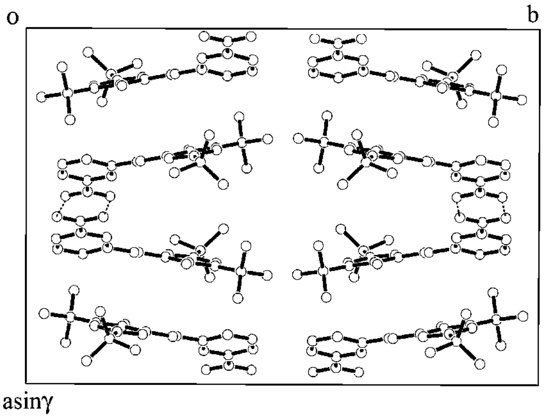


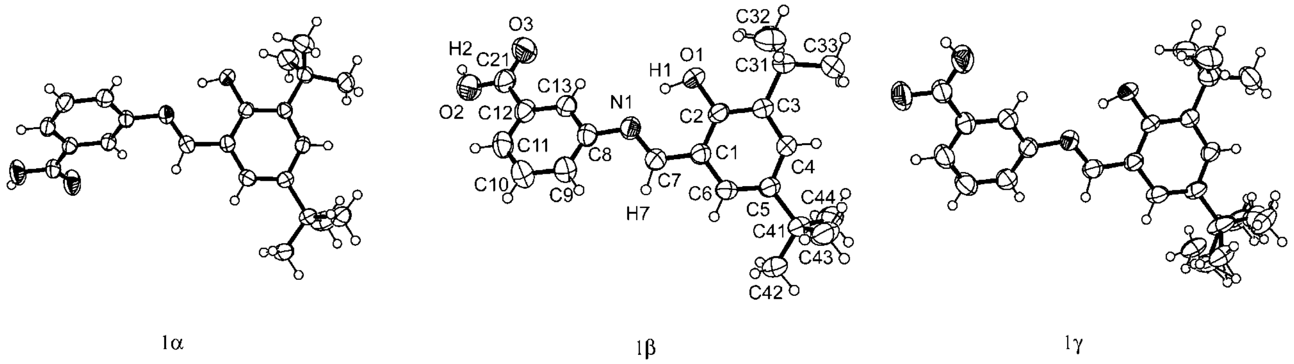
Figure 4. Crystal structure of **1*γ*** viewed along the *c* axis.

Table 3. The Intermolecular Hydrogen Bond Distances and Angles of the Three Crystals

	1*α*	1*β*	1*γ*
O2–O3/Å	2.6637(18)	2.630(2)	2.6555(17)
H2···O3/Å	1.85	1.82	1.33
O2–H2–O3/°	175	168	180

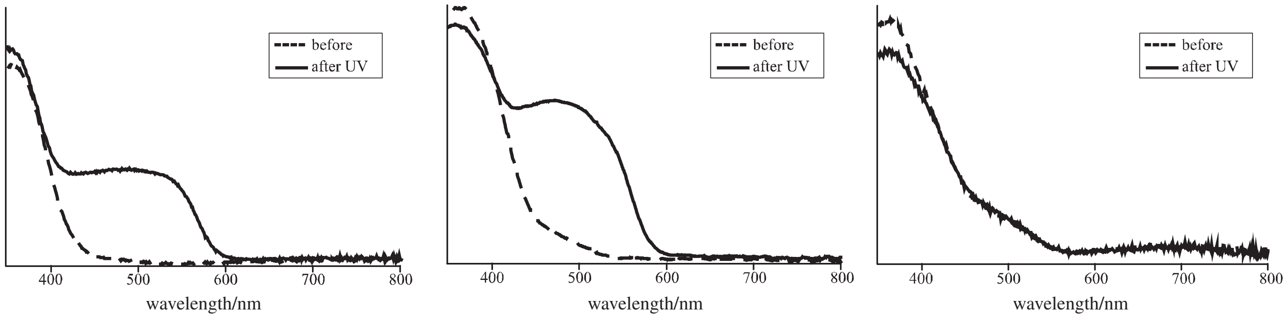
Table 4. Selected Bond Distances and Angles and Torsion Angles of the Three Crystals before Irradiation

	1*α*	1*β*	1*γ*
C1–C7/Å	1.4557(19)	1.452(2)	1.452(2)
C7–N1/Å	1.2762(18)	1.281(2)	1.2791(19)
N1–C8/Å	1.4259(17)	1.4171(19)	1.4196(19)
C1–C7–N1/°	123.43(13)	122.48(15)	122.65(15)
C7–N1–C8/°	118.36(12)	120.43(14)	121.85(13)
O1···N1/Å	2.6254(15)	2.5911(19)	2.5848(17)
H···N1/Å	1.77(2)	1.68(2)	1.67(2)
O1–H–N1/°	150.9(19)	151.8(18)	157.7(18)
O3–C21–C12–C13/°	−2.9(2)	−5.3(3)	1.2(2)
C1–C7–N1–C8/°	176.32(13)	−178.42(13)	180.00(14)



1α 1β 1γ

Figure 5. Molecular structures of the three forms, **1*α***, **1*β***, and **1*γ***. The thermal ellipsoids are drawn at 50% probability level.



(a) (b) (c)

Figure 6. UV–vis spectra of (a) **1*α***, (b) **1*β***, and (c) **1*γ*** before (dotted) and after (solid) photoirradiation. Absorbance is taken in an arbitrary scale. Subsequent visible irradiation gave the same spectra as those before irradiation.

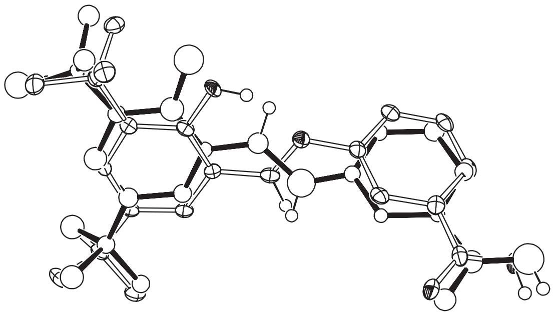


Figure 7. Disordered structure of **1*α*** after UV irradiation (365 nm). The bonds of the enol and *trans*-keto forms are drawn in white and black, respectively. The thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms of phenyl and *t*-butyl groups are omitted for clarity.

The lifetimes of the colored species for **1*α*** and **1*β*** were estimated to be 17 and 780 min, respectively, from the changes of their IR spectra and were compared with the corresponding lifetime (1200 min) of **2**. Although it was reported that **2** has a lifetime of 40 days from the change of the UV reflectance spectra,[5] the lifetime seems to depend strongly on the measurement methods.

Crystal and Molecular Structure of 1*α* after Photoirradiation. The structure of a thin **1*α*** crystal after photoirradiation was analyzed at 93 K. The unit-cell lengths of *a* and *c* are slightly expanded due to the formation of the photo colored species in the crystalline lattice. The molecular structure is shown in Figure 7. In addition to the original enol form, the *trans*-keto form appeared as a disordered structure. This structure clearly indicates that the photo colored species is the *trans*-keto form, which was also shown in the photo colored crystal of **2**. The peripheral groups of the molecule, two *tert*-butyl and carboxyl groups occupy nearly the same positions as those before irradiation and the intermolecular hydrogen bonds between the hydroxy groups are conserved in the photoreaction. This is the reason why the photoreaction proceeded without destroying the single crystal form. The transformation from the enol to *trans*-keto form is well explained by pedal (crankshaft) motion[13] keeping the two phenyl rings in similar positions as observed in the photoreaction of crystal **2**.

Intermolecular Hydrogen Bond Formation in the Photo Colored Crystals. In the structure analysis of the photo colored crystal of **2**, we found that intermolecular hydrogen bonds were formed between the N–H group of the *trans*-keto imine group and the oxygen atom of the nitro group around an inversion center and a dimer structure was formed around the inversion center as shown in Figure 8. It was theoretically proposed that the intermolecular hydrogen bond is responsible for the stabilization of the *trans*-keto form and that the longest lifetime of the photo colored species comes from the stabilization energy due to the hydrogen bond formation, $-39.36\,\mathrm{kJ\,mol^{-1}}$.[8]

In order to compare the structure of the photo colored species of **1*α*** with that of **2**, the two produced *trans*-keto forms around an inversion center are shown in Figure 9. The N–H group of the imine group is surrounded by the methyl groups of the *tert*-butyl group of the neighboring molecule. No hydrogen bond is newly made in the structure. This is why the photo colored species of **1*α*** has a shorter lifetime (17 min) than that of the photo colored species of **2** (1200 min).

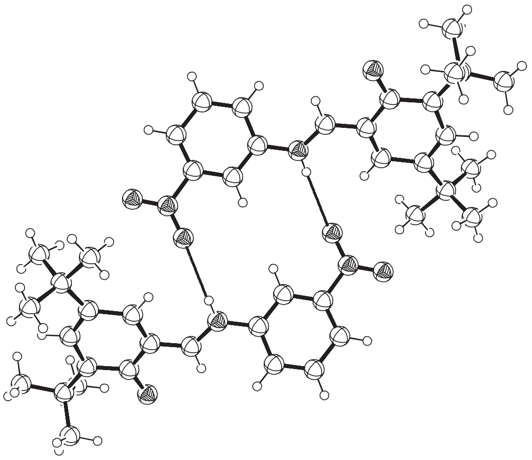


Figure 8. Intermolecular hydrogen bond formation of the *trans*-keto form in the colored species of **2**. The atoms of enol form are omitted for clarity.

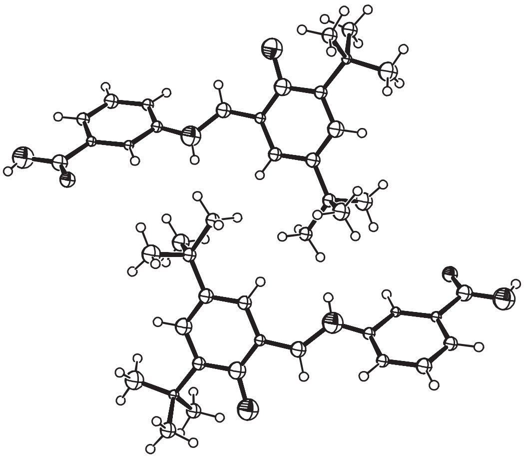


Figure 9. Intermolecular contact of the *trans*-keto form with the neighboring molecule in the colored species of **1*α***. The atoms of enol form are omitted for clarity.

Although it was impossible to obtain the structure of the photo colored species for **1*β*** because of the smaller occupancy factor of the produced *trans*-keto form than that of **1*α***, it seems adequate to assume that the *trans*-keto form has essentially the same structure as that of **1*α*** and **2**, which are produced using the pedal motion. The molecular structure of the *trans*-keto form was situated in the crystal of **1*β***. It was found that the N–H group of the produced *trans*-keto form makes a hydrogen bond with the oxygen atom of the carboxyl group of the neighboring molecule, as shown in Figure 10. The N···O distance and N–H···O angle are 2.8 Å and 110°, respectively. These values suggest that a fairly strong hydrogen bond may be made between these atoms. This may be why **1*β*** has a longer lifetime than **1*α***. The hydrogen bond will make a ribbon if all the molecules in **1*β*** will are changed to the *trans*-keto form. However, such a ribbon may be difficult to make in the crystalline lattice, since the occupancy factor is less than 0.1.

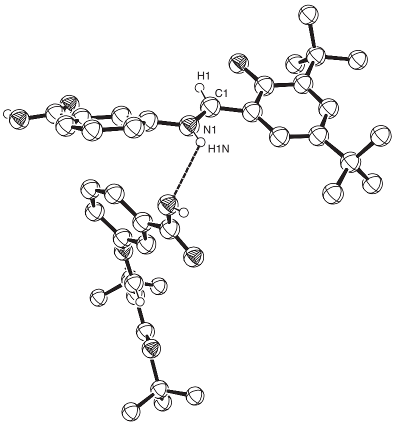


Figure 10. Estimated hydrogen bond formation of the *trans*-keto form of **1*β***.

Therefore the *trans*-keto form of **1*β*** may not be so effectively stabilized. On the other hand, since the dimer of the *trans*-keto form of **2** may be easily made even if the total occupancy factor of the *trans*-keto form is not so large (ca. 0.1), the *trans*-keto form may be largely stabilized. This may be why the lifetime of **2** (1200 min) is significantly longer than that of **1*β*** (780 min).

Cavity for the Pedal Motion. It was proposed that the transformations from the enol to *trans*-keto form and from the *trans*-keto to enol form occur through the pedal motion.[13] This indicates that the largest atomic shifts before and after the photoreaction should occur in the imine group connecting the two phenyl rings in the salicylideneaniline molecule. The greater the void space around the imine group, the easier the transformation. It seems adequate to assume that the stability of the *trans*-keto form should depend on the void space around the imine group, that is, the size of the reaction cavity for the imine group.[14] The reaction cavity for the imine group was calculated for the *trans*-keto forms of **1*α***, **1*β***, and **2**, which are shown in Figure 11. The size of the cavity was calculated to be 3.5, 1.6, and 1.3 Å^3 for **1*α***, **1*β***, and **2**, respectively. These values are in good agreement with their lifetimes observed by the IR spectra. The cavity size for the imine group also plays an important role for the lifetime of the photo colored crystal, although the effect may be smaller than that of the intermolecular hydrogen bond formation of the produced N–H group, considering the stabilization energy.

Non-Photoreactivity of 1*γ*. It was claimed that the dihedral angle between two phenyl rings of the salicylideneaniline molecule plays an important role in showing photochromic properties.[15] The salicylideneaniline crystal with larger dihedral angle shows the photochromic properties. We crystallized 24 kinds of salicylideneaniline compounds. Crystals with dihedral angles less than 25° were non-photochromic whereas those with dihedral angles more than 45° were photochromic. Crystals with dihedral angles between 25 and 45° are either photochromic or non-photochromic.[16] The dihedral angles for **1*α***, **1*β***, and **1*γ*** are 60.95, 37.34, and 28.90°, respectively. This indicates that **1*α*** would show photochromicity but that **1*β*** may be either photochromic or non-photochromic. The **1*γ*** crystal may be non-photochromic since the dihedral angle is very close to the limiting value for the non-photochromic crystals. This well explains the photochromic properties for the above three polymorphic crystals. However, it was recently reported that crystals with a dihedral angle more than 80° are non-photochromic.[6] The relationship between the dihedral angle and photochromism will be discussed in the future.

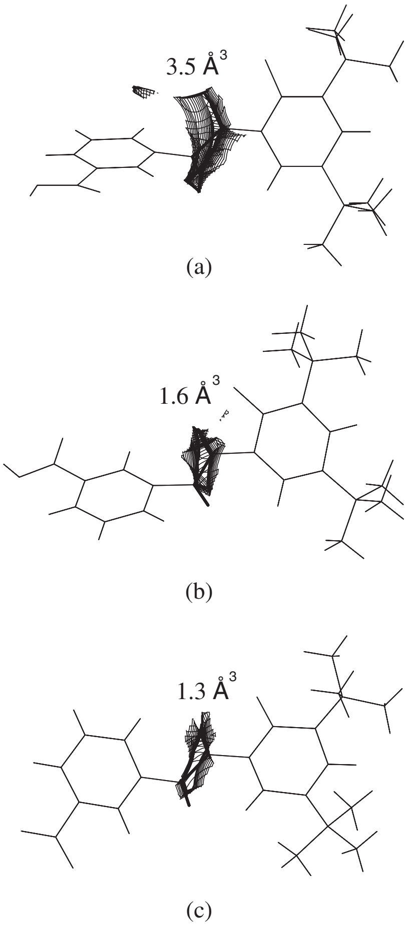


Figure 11. Reaction cavities around the imine (–NH–CH–) functionality of the *trans*-keto forms of photochromic (a) **1*α***, (b) **1*β***, and (c) **2**.

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