Photochromism of polymorphic 4,4′-methylenebis-(N-salicylidene-2,6-diisopropylaniline) crystals

Masatsugu Taneda, Kiichi Amimoto, Hiroyuki Koyama and Toshio Kawato *

Department of Chemistry, Faculty of Sciences, Kyushu University, 4-2-1 Ropponmatsu, Chuo-ku, Fukuoka 810-8560, Japan. E-mail: kawato@chem.rc.kyushu-u.ac.jp
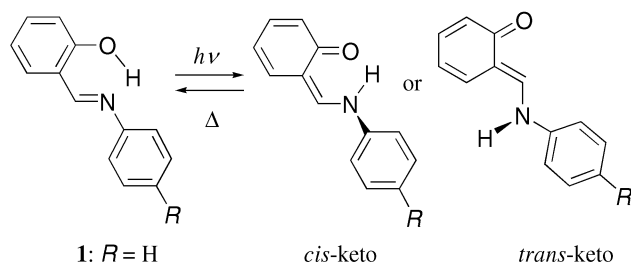
4,4′-Methylenebis(N-salicylidene-2,6-dialkylaniline) derivatives were prepared and their structures were determined by ^{1}H NMR, IR, DSC and X-ray crystallographic analyses. The 2,6-diisopropylaniline derivative yielded definite polymorphic crystals: the space groups of the crystals were $C2/c$ and $P2_1/n$, respectively. It was found that both polymorphs were similarly photochromic but the thermal stability of the photochrome was different due to the variance of the shape of molecule and cavity in each crystal.

Introduction

Solid-state photochromism has been the subject of resurgent interest due to the potential applications.[1] N-Salicylideneamine (**1**) and its derivatives are well known to exhibit either photochromism or thermochromism in the crystal state irrespective of the chemical properties of their ring substituents (Fig. 1); therefore, topochemical problems exist in the phenomena.[2] For a better understanding of the chemistry of organic crystals it is sometimes effective to study the same reaction in more than one crystalline modification or polymorphic form.[3] Any reactivity differences that are noted between polymorphs can frequently be ascribed to the structural differences, thereby allowing a deeper insight into the relationship between structure and reactivity in organic photochemistry.[4] Although there is no definite method available to crystallize with the required packing,[5] polymorphs may differ from one another not only in their packing arrangements but also in subtle variations in the conformations of the constituent molecules. Such a strategy allows the design of potential polymorphic Schiff base crystals. For example, 4,4′-methylenebis(N-salicylideneaniline) (**2**)[6] and its analogues can exhibit conformational or bond-rotational flexibility at the central methylene group which links two photochromic N-salicylideneanilines to demonstrate the difference in crystal structure, *syn*-form and *anti*-form (Fig. 2). In order to explore this possibility we prepared photochromic 4,4′-methylenebis(N-salicylidene-2,6-dialkylaniline) derivatives and determined the structure of the resultant crystals. The purpose of this paper is to report the results of our studies on the correlation between crystal structure and photochromic properties of Schiff base polymorphs.
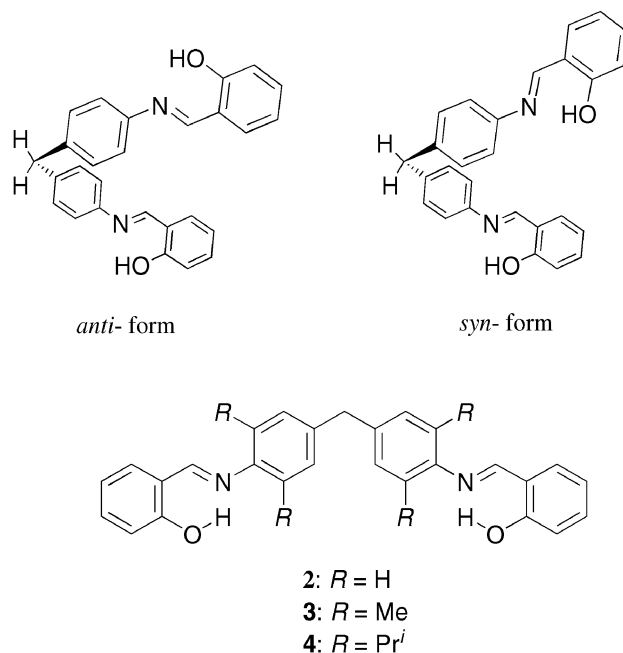

Fig. 2 Schematic representation of conformational isomers of 4,4′-methylenebis(N-salicylideneaniline) (**2**) and its derivatives studied.

Results and discussion

The desired Schiff base dimer **2** was prepared by the usual condensation of salicylaldehyde with bis(4-aminophenyl)methane in methanol. Since the obtained crystal did not exhibit photo-colouration,[7] we did not study the compound further but we decided to introduce 2,6-dialkyl substituents to the aniline rings of **2**. Recently we revealed that steric repulsion between the azomethine hydrogen atom and the alkyl groups at the 2,6-positions of the aniline ring of **1** and its derivatives lead to a non-planar molecular structure, which was effective for the crystals to exhibit photochromism.[8] Thus, 2,6-dimethylaniline derivative (**3**) and 2,6-diisopropylaniline analogue (**4**) of **2** were prepared to yield photochromic crystals satisfactorily (Fig. 2). The resultant crude products were purified by recrystallization from common organic solvents to give pure samples as yellow crystals. In the case of **3**, only one form of crystal was yielded, while compound **4** was found to produce two types of crystals, **4α** and **4β**.

Crystal **4α** was a yellowish thin plate, which was obtained by recrystallization from methanol. Crystal **4β** was attained as a

Fig. 1 Photochromic reaction of N-salicylideneanilines.

R = H, Br, C(CH₃)₃ : photochromic
R = F, Cl, CH₃, OCH₃ : non-photochromic

Table 1 Crystal data of **3**, **4α** and **4β**

Data	3	4α	4β
Formula	$C_{31}H_{30}N_2O_2$	$C_{39}H_{46}N_2O_2$	$C_{39}H_{46}N_2O_2$
Formula weight	462.57	574.80	574.80
Crystal size/mm	$0.40 \times 0.30 \times 0.20$	$0.40 \times 0.30 \times 0.10$	$0.30 \times 0.30 \times 0.20$
Temperature/K	296	296	296
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$C2/c$	$P2_1/n$
a/Å	9.947(1)	36.700(4)	18.991(4)
b/Å	11.658(2)	8.747(4)	6.010(4)
c/Å	12.796(1)	10.687(4)	31.619(4)
α	67.062(9)°	90°	90°
β	82.79(1)°	92.62(2)°	103.22(1)°
γ	70.76(1)°	90°	90°
V/Å³	1290.2(3)	3426.9(2)	3512.9(3)
Z	2	4	4
D_{calc}/g cm⁻³	1.191	1.114	1.087

yellow column by recrystallization from acetonitrile containing a small amount of water. Both **4α** and **4β** were confirmed to have the same composition by elemental analyses. Their ^{1}H NMR spectra in CDCl$_3$ were the same, which shows that the structure of the molecules in the two crystals was identical in solution. On the other hand, the melting points of **4α** and **4β** were 157 °C and 173 °C, respectively. The differential scanning calorimetric analyses (DSC) were carried out to elucidate the distinction of the crystalline phase between **4α** and **4β**. The DSC curve for **4β** showed only one endothermic peak (T_m = 173 °C) due to the melting of the crystal, whereas two endo-thermic peaks (T_m = 157 °C and 172 °C) and one exothermic peak (T_m = *ca.* 165 °C) appeared in the DSC curve for **4α** (Fig. 3). This result suggested that the metastable crystal lattice of **4α** was destroyed at around 157 °C, then transformed into the stable crystalline phase of **4β** and melted finally at the melting point of **4β**. Infrared spectra of **4α** and **4β** were almost super-imposable upon each other except some peaks at around 1280 cm⁻¹ due to C–O stretching vibration and at near 830 cm⁻¹ due to C–H out-of-plane vibration. In this study, polymorphism was expected to be concerned with the existence of two molecu-lar isomeric forms, *i.e. syn*-form and *anti*-form, in the crystal state. In order to confirm this, the crystal structures of **3**, **4α** and **4β** were determined by X-ray structural analysis.
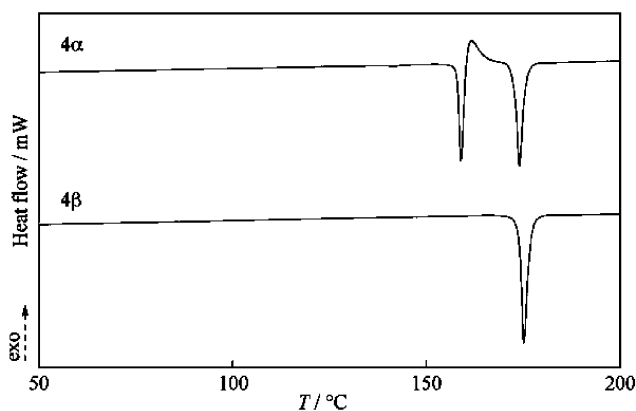
Fig. 3 DSC curves of **4α** (top) and **4β** (bottom).

Crystal structure of 4,4′-methylenebis(*N*-salicylidene-2,6-dimethylaniline) (3) and 4,4′-methylenebis(*N*-salicylidene-2,6-diisopropylaniline) polymorphs (4α and 4β)

The crystal data are shown in Table 1. The crystal structure of **3** was found to be disordered by two presumed orientations of molecules. In other words, both *syn*-form and *anti*-form coexist equally in one single crystal. Table 2 lists the observed bond lengths, which exhibit phenol-imine structure for the *N*-salicyl-ideneamine parts of **3** before photo-isomerization. The uni-molecular structure in the crystal is shown in Fig. 4. In the
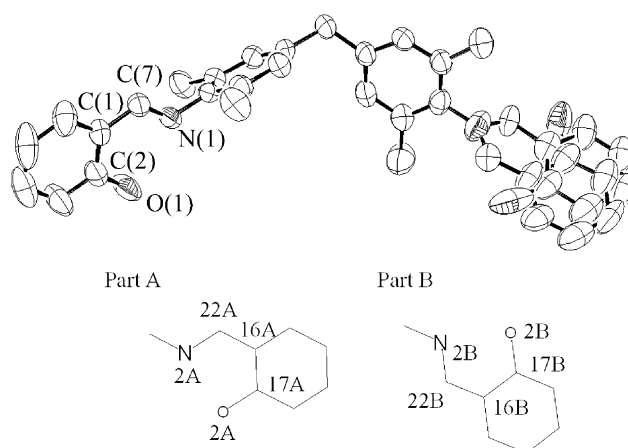
Fig. 4 Disordered molecular structure of **3** with the numbering scheme. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are not drawn for clarity. The schematic drawings of the disordered parts A and B are shown on the bottom of the ORTEP drawing with the numbering scheme.

crystal lattice of **3**, one salicylidene moiety may take either orientation to shape *syn*-form or *anti*-form in a relatively large cavity between two aminoaromatic rings of the neighbouring molecule. Thus, it seems to make almost no difference in the lattice energy whether the crystal is constructed by both *syn*-formed molecules and *anti*-formed molecules or by either one of them exclusively. This small potential energy gap might be the reason polymorphs of **3** could not be isolated.[9]

In the case of **4**, the situation is a little different. Bulky iso-propyl substituents in **4** might fill the cavity in the crystal lattice to make the different lattice energy under consideration. As a result, polymorphic crystals, **4α** and **4β**, could be isolated. X-Ray crystallographic analyses of **4α** and **4β** revealed the structural difference between the two polymorphs clearly. The space group of **4α** was $C2/c$ ($Z = 4$) with a center of symmetry, whereas the crystal system of **4β** was $P2_1/n$ ($Z = 4$). The unit cell volumes of **4α** and **4β** were 3426.9 Å³ and 3512.9 Å³, respect-ively. According to the bond lengths (Table 2), the molecular structure of **4** is essentially represented as a phenol-imine form. The unimolecular structures of **4α** and **4β** are shown in Fig. 5; the unit molecule in **4α** takes the *anti*-form, while that of **4β** takes the *syn*-form.

Photochromism of 4,4′-methylenebis(*N*-salicylidene-2,6-diisopropylaniline) (4) polymorphs

Both **4α** and **4β** crystals were photochromic. By irradiating the yellowish crystalline samples with 365 nm light, the colour turned to orange, which returned slowly to the original yellow in the dark. The reflectance spectra of **4α** and **4β** before and after UV irradiation are shown in Fig. 6. Since the

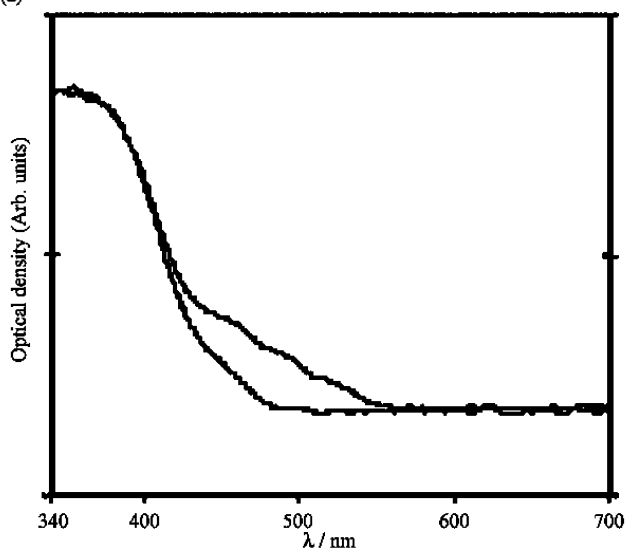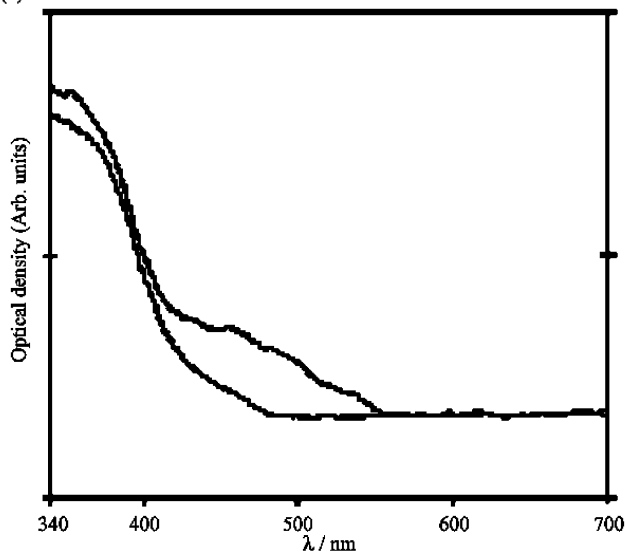**Table 2** Selected bond lengths of **3**, **4α** and **4β** (/Å)

	3		4α		4β	
	O(1)–C(2)	1.337(6)	O(1)–C(2)	1.342(4)	O(1)–C(2)	1.36(1)
	C(1)–C(2)	1.392(5)	C(1)–C(2)	1.390(5)	C(1)–C(2)	1.38(1)
	C(1)–C(7)	1.452(4)	C(1)–C(7)	1.459(4)	C(1)–C(7)	1.45(1)
	N(1)–N(7)	1.267(4)	N(1)–C(7)	91.280(3)	N(1)–C(7)	1.27(1)
	O(2A)–C(17A)	1.37(2)			O(2)–C(21)	1.36(1)
	C(16A)–C(17A)	1.35(2)			C(20)–C(21)	1.40(1)
	C(16A)–C(21A)	1.41(2)			C(20)–C(26)	1.46(1)
	N(2)–C(22A)	1.080(8)			N(2)–C(26)	1.26(1)
	O(2B)–C(17B)	1.36(2)				
	C(16B)–C(17B)	1.44(2)				
	C(16B)–C(21B)	1.44(2)				
	N(2)–C(22B)	1.107(7)				

Table 3 Rate constants k (30 °C) of thermal fading reaction of photo-coloured species measured at the optimum wavelength λ

Crystal	λ/nm	k_1/s^{-1}	k_1/s^{-1}	k_2/s^{-1}
4α	459.2	1.4×10^{-4}		6.8×10^{-5}
4β	466.8	2.1×10^{-3}	9.2×10^{-5}	3.8×10^{-5}
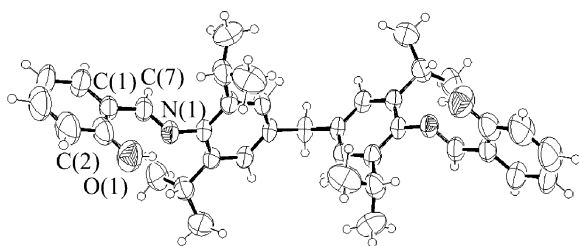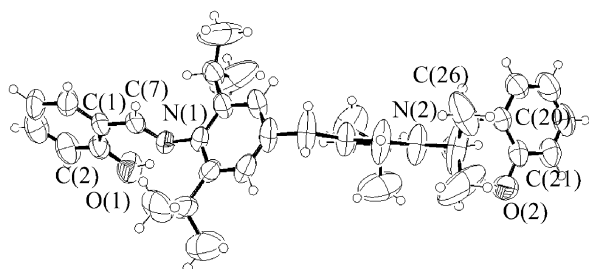
Fig. 5 Molecular structures of **4α** (top) and **4β** (bottom) with the numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

Fig. 6 Solid state reflectance spectra of **4α** (a) and **4β** (b) before and after UV irradiation.

corresponding spectra of these samples were closely similar, it was supposed that there was no essential difference between the photochromic processes of the polymorphs. The thermal fading reaction of the photoproduct was then monitored by the decreasing rate of absorption band due to the photo-coloured species. Detailed kinetic measurements and calculations of the rate constants k were described in a previous paper.[10] Kinetic analysis for **4α** and **4β** exhibited a good fit to a first-order equation. The constructed first-order plots for **4α** consisted of a two-stage transient decay (Fig. 7); the first-order or pseudo-first-order rate constants ($k_{1(4\alpha)}$ and $k_{2(4\alpha)}$ for the first and second steps) could be obtained. On the other hand, the data of **4β** indicated three rate constants (Fig. 7), which were represented as $k_{1(4\beta)}$, $k_{1'(4\beta)}$ and $k_{2(4\beta)}$ because double first steps were supposed to occur for **4β** due to its unsymmetrical molecular structure as described below. The cycle of photo-colouration and thermal decolouration in this study was repeated many times without any side reaction. Since the degree of colour change and the rate constants measured were intact for the repeated experiments, the compounds seemed to remain at the same degree of crystallinity during the photo-isomerization. The obtained reaction rate constants are summarized in Table 3.

It is generally accepted that the photo-colouration of Schiff bases involves an intramolecular proton transfer from the *o*-hydroxyl group to the imine nitrogen atom in the excited state followed by the intramolecular framework alteration. Recent studies have demonstrated the existence of two photo-coloured species, the *cis*-keto form[11] and the *trans*-keto form,[12] in the crystals (Fig. 1). We now start to study the thermal relaxation reaction of the photo-coloured species in the polymorphic form.
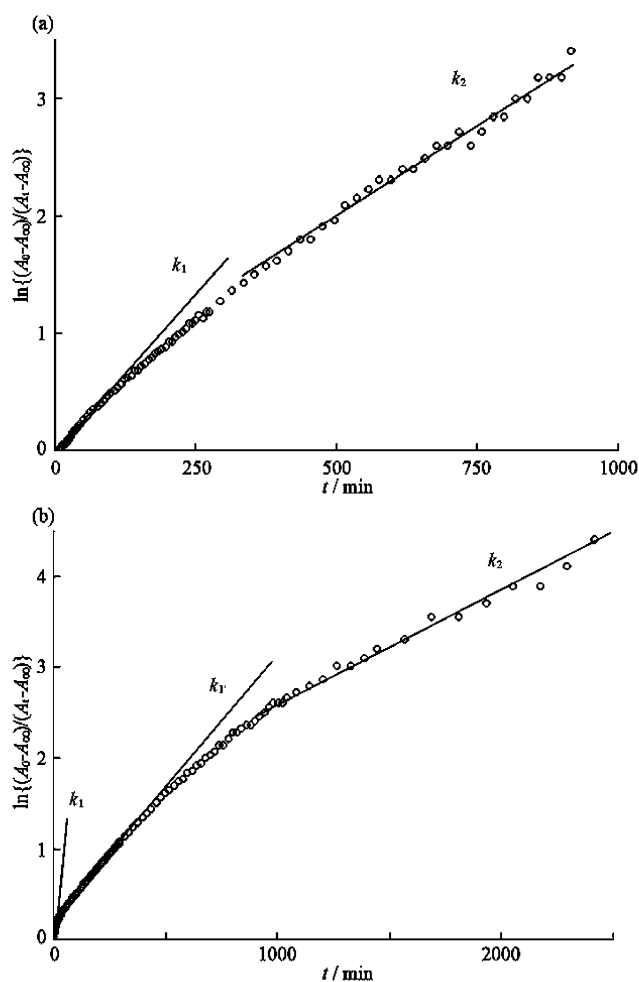
Fig. 7 Kinetic plots of optical density decrease for the photo-coloured species derived from **4α** (a) and **4β** (b).

Correlation between crystal structure and stability of photochromes

Since the thermal fading process of photochromes of *N*-salicylideneanilines contains transformation of molecular structure in the crystal state, the rate of thermal bleaching reaction might be profoundly related to the size of cavity around the reaction center. In this study the reaction room around salicylideneamine moiety must be critical: thus, the crystal structure of two polymorphs was studied in further detail. Packing diagrams of **4α** and **4β** are shown in Fig. 8 and Fig. 9, respectively. As we would expect in both crystals the isopropyl substituents at the 2- and 6-positions of the aniline rings play important roles in deciding the shape and size of cavity. They are in contact with each of the neighbouring molecules and/or situated on the adjoining salicylidene-aromatic ring. In contrast with the crystal structure of **3**, there is not enough room between the amino-aromatic rings to adapt to the salicylidene moieties. Because of the symmetry of the molecule, there is just one type of salicylidene moiety (Sα) in **4α** (C_2 symmetry), whereas two kinds of salicylidene moieties (Sβ and Sβ′) exist in **4β**. According to the literature method,[13] the mass volume of each cavity around the

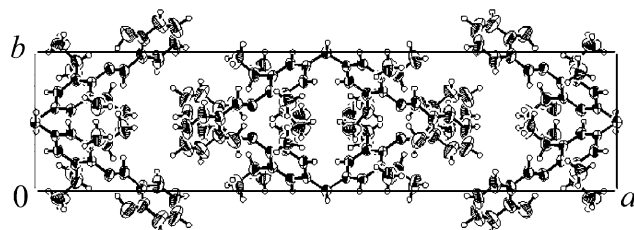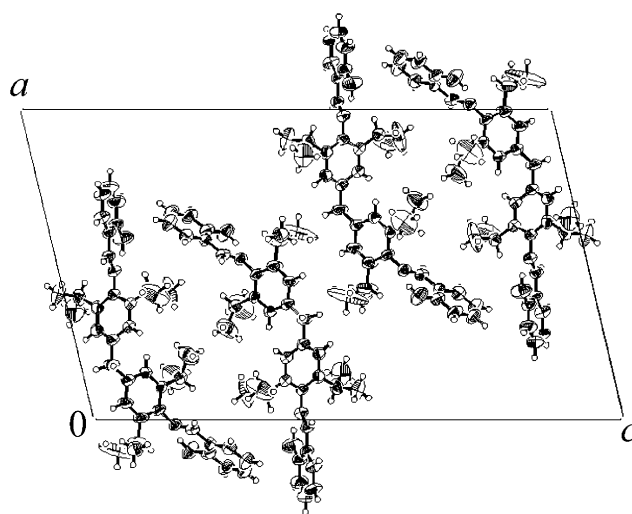**Fig. 8** Packing diagram of **4α** along the *c* axis.

salicylideneamine moiety for Sα, Sβ and Sβ′ was calculated to be 27.4, 25.4 and 28.4 Å^3, respectively. Since the assignment of the reaction rate constant $k_{(4β)}$ due to Sβ and Sβ′ or the correlation of the rate constant with the cavity is tentative, we cannot discuss this in further detail. However, it is worthwhile to note that the decreasing order of the cavity size, Sβ′ > Sα > Sβ, agrees with the order of the rate constants for initial step, $k_{1'(4β)}$, $k_{1(4α)}$ and $k_{1(4β)}$, which decrease in this order according to the provisional assignment in Table 3.

In our previous study it was considered that two consecutive first-order decays of the photo-coloured species were ascribed to the framework relaxation of two types of quinoid-amine form to the original phenol-imine form in the ground state.[11] In the paper the initial fading step (rate constant: $k = k_1 - k_2 \approx k_1$) was attributed to the thermal back reaction of the *cis*-keto form that was generated by the photo-irradiation and existed in the initial photo-coloured crystals to a certain extent. Assuming these to be correct, the explanation given earlier with respect to the stability of the photochrome is applicable.[10] The molecular deformation that is constrained by photo-irradiation in the crystal lattice must cause a new steric repulsion due to the induced contact with the neighbouring molecules. If the cavity around the reaction center is small, the photo-coloured species must be in a high energy state due to the repulsive interaction. This instability of the photoproduct leads to a low potential energy barrier of thermal relaxation, making the reaction fast.

Although the existence of a *trans*-keto form is ascertained as a photoisomer of a monomeric Schiff base,[12] the origin of the second fading step in this study is rather vague. Due to the increased difficulty of geometrical changes for such a dimeric Schiff base the slower stage may not be able to impute to the thermal back reaction of the *trans*-keto form. The relaxation of the crystal lattice involving a molecular framework variation may be another probable interpretation for the second stage of thermal bleaching. The photo-isomerization process might involve rotation around the aminoaromatic carbon–nitrogen bond or other molecular transition to stabilize the resultant *ortho*-quinoid-amine form in the crystal lattice.

In any case, this second step might correlate to a motion of the whole molecule and require a large reaction room in the crystal lattice. In order to inspect the degree of molecular packing in a crystal, densities of crystals were calculated to be 1.114 g cm^{-3} for **4α** and 1.087 g cm^{-3} for **4β**, respectively. Small crystal density is associated with an open crystal structure for **4β**, whose final rate constant $k_{2(4β)}$ is smaller than that of **4α**, $k_{2(4α)}$. This tendency is explicable in the same manner as the explanation for the order of initial rate constants k_1 described above.

Fig. 9 Packing diagram of **4β** along the *b* axis.

Conclusion

The bis(*N*-salicylideneaniline) method in this study was suggested to be effective to prepare polymorphic crystals and the 2,6-dialkylaniline method in the literature[8] was confirmed to be effective to prepare photochromic crystals. Thus, 4,4′-methylenebis(*N*-salicylidene-2,6-diisopropylaniline) yielded definite photochromic polymorphs. This is the first report in which both structures of two polymorphs of photochromic *N*-salicylideneaniline derivatives were determined. Since the difference of reactivity of polymorphs was ascribed to the distinction of crystal structure, we could discuss the relationship between structure and stability of the photo-coloured species of Schiff bases. Although the mechanism of the thermal fading process of the photo-isomerized Schiff bases could not be defined clearly, it was probably safe to suggest that the thermo-isomerization reaction was slower in a larger cavity around the reaction center in the crystal lattice. Further work needs to be done on this interesting system to permit the deduction of a reasonable reaction mechanism. We are currently preparing analogous Schiff base dimers to elucidate further the photochemical reactions.

Experimental

General comments

All melting points (mp) were measured by a YAMATO model MP-21 melting point apparatus and are uncorrected. IR absorption spectra were recorded using a JASCO FT/IR-420 spectrometer. UV/VIS spectra were measured by a JASCO UVIDEC-650 spectrometer. ^{1}H NMR spectra were determined on a JEOL GSX-270 FT NMR spectrometer with CDCl$_3$ as solvent and TMS as internal standard ($\delta = 0$ ppm). Differential scanning calorimetric measurement (DSC) was carried out using a Shimadzu DSC-50 apparatus at a heating rate of 5 °C min^{-1} under N$_2$ gas. Elemental analyses were performed by the Service Center of the Elementary Analysis of Organic Compounds affiliated to the Faculty of Sciences in Kyushu University.

4,4′-Methylenebis(*N*-salicylideneaniline) (2)

Salicylaldehyde (0.736 g, 6.03 mmol) was added to the solution of bis(4-aminophenyl)methane (0.591 g, 2.98 mmol) in methanol (15 ml) and the mixture was stirred at room temperature for 5 min. After the solution was concentrated, the resultant precipitate was filtered and recrystallized from a mixture of methanol and acetone to afford yellow fine crystals of **2** (1.01 g, 83.3%). Mp: 211.5–212.0 °C (lit. 116–117 °C and 216 °C[6,7]) (Found: C, 79.80; H, 5.51; N, 6.87%. C$_{27}$H$_{22}$N$_2$O$_2$ requires C, 79.78; H, 5.46; N, 6.89%).

4,4′-Methylenebis(*N*-salicylidene-2,6-dimethylaniline) (3)

Salicylaldehyde (0.726 g, 5.97 mmol) was added to the solution of 4,4′-methylenebis(2,6-dimethylaniline) (0.766 g, 3.01 mmol) in methanol (20 ml) and the mixture was stirred at room temperature for 5 min. After the solution was concentrated, the resultant precipitate was filtered and recrystallized from a mixture of methanol and acetone to afford yellow fine crystals of **3** (0.627 g, 45.4%). Mp: 130.0–130.5 °C (Found: C, 80.44; H, 6.54; N, 6.02%. C$_{31}$H$_{30}$N$_2$O$_2$ requires C, 80.49; H, 6.54; N, 6.06%); δ_H(270 MHz; CDCl$_3$): 2.08 (12H, s, Ar-CH$_3$), 3.91 (2H, s, Ar-CH$_2$-Ar), 6.95–7.08 (8H, m, Ar-H), 7.36 (4H, m, Ar-H), 8.32 (2H, s, CH=N), 13.16 (2H, b, Ar-OH).

4,4′-Methylenebis(*N*-salicylidene-2,6-diisopropylaniline) (4)

Salicylaldehyde (0.737 g, 6.04 mmol) was added to the solution of 4,4′-methylenebis(2,6-diisopropylaniline) (1.170 g, 3.19 mmol) in methanol (20 ml) and the mixture was stirred at room temperature for 5 min. After the solution was concentrated, the

resultant precipitate was filtered and recrystallized from a mixture of methanol and acetone to afford yellow fine crystals as a mixture of **4α** and **4β** (0.925 g, 53.3%). Mp 166.0–168.0 °C; δ_H(270 MHz; CDCl$_3$): 1.16 (24H, d, J = 6.7 Hz, (C*H*$_3$)$_2$CH), 3.03 (4H, dq, J = 6.7, (CH$_3$)$_2$C*H*), 4.07 (2H, s, Ar-CH$_2$-Ar), 7.05–7.10 (8H, m, Ar-H), 7.33–7.48 (4H, m, Ar-H), 8.31 (2H, s, CH=N), 13.19 (2H, b, Ar-OH).

Crystal **4α** was obtained by recrystallization from methanol as yellowish thin plates. Mp 157.0–158.0 °C (Found: C, 81.49; H, 8.07; N, 4.88%. C$_{39}$H$_{46}$N$_2$O$_2$ requires C, 81.49; H, 8.07; N, 4.87%).

Crystal **4β** was obtained by recrystallization from acetonitrile containing a small amount of water as yellow columns. Mp 173.0–173.5 °C (Found: C, 81.55; H, 8.06; N, 4.87%. C$_{39}$H$_{46}$N$_2$O$_2$ requires C, 81.49; H, 8.07; N, 4.87%).

Photo-colouration measurement

Crystalline powders of Schiff bases were placed between two glass plates and were stored in the dark at 30 °C before the measurements were carried out. Photo-colouration was accomplished by irradiating the sample with 365 nm light using a hand-held UV lamp (UVP MINERALIGHT® LAMP UVGL-25). Electronic reflectance spectra were monitored by a JASCO UVIDEC-650 spectrometer.

X-Ray crystallography †

Single crystals suitable for X-ray diffraction were obtained by recrystallization from ethanol (**3**), methanol (**4α**) or acetonitrile with a small amount of water (**4β**). Each crystal was mounted at the end of a glass fiber and coated with epoxy resin. X-Ray diffraction experiments were performed on a Rigaku AFC7R X-ray diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71069 Å) and a rotating anode generator. A brief summary of crystal data and refinement parameters is given in Table 1. For **3** including disordered components, all calculations were performed by the WinGX software package.[14] The structure was solved by direct methods using SHELXS-97[15] and refined by full matrix least-squares on F^2 with SHELXL-97.[15] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically except those fitted on carbon atoms of the disordered parts, which were fixed geometrically and not refined. For the two polymorphs, **4α** and **4β**, structure solution and refinement were carried out with the CrystalStructure™ crystallographic software package.[16] The structure was solved by direct methods using SHELXS-97[15] and refined by full matrix least-squares on F with a Sheldrick weighting scheme. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model.

2,6-Dimethylaniline derivative (3)

Of the 5345 reflections which were collected, 5067 were independent (R_{int} = 0.0509); equivalent reflections were merged. The linear absorption coefficient, μ, for Mo-Kα radiation is 0.074 mm^{-1}. The extinction coefficient was refined to 0.050(10). The structure was refined on F^2 with 483 parameters to R_1 0.0621, wR_2 0.1848 for 2214 reflections with $I > 2\sigma(I)$ and R_1 0.166, wR_2 0.2651 for all data. The salicylidene moiety at the N2 atom was found to be disordered. Two orientations of this part were included in the model with occupancies of 0.50 and 0.50.

anti-Formed 2,6-diisopropylaniline derivative (4α)

Of the 4252 reflections which were collected, 3930 were independent (R_{int} = 0.042); equivalent reflections were merged. The

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intensities of three representative reflections were measured after every 150 reflections. Over the course of data collection, the standards decreased by 2.6%. A linear correction factor was applied to the data to account for this phenomenon. The linear absorption coefficient, μ, for Mo-Kα radiation is 0.068 mm^{-1}. The structure was refined on F with 221 parameters to R_1 0.049, Rw 0.058 for 1558 reflections with $I > 3\sigma(I)$.

syn-Formed 2,6-diisopropylaniline derivative (4β)

Of the 6066 reflections which were collected, 5266 were independent (R_{int} = 0.663); equivalent reflections were merged. The intensities of three representative reflections were measured after every 150 reflections. Over the course of data collection, the standards decreased by 0.4%. A polynomial correction factor was applied to the data to account for this phenomenon. The linear absorption coefficient, μ, for Mo-Kα radiation is 0.066 mm^{-1}. The structure was refined on F with 435 parameters to R 0.076, Rw 0.104 for 1907 reflections with $I > 3\sigma(I)$.

Acknowledgements

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