Journal of Photochemistry, *28* (1985) 103 - 110

PHOTOISOMERIZATION AND THERMOISOMERIZATION I: UNUSUAL PHOTOCHROMISM OF *N*-(3,5-DI-*tert*-BUTYLSALICYLIDENE)AMINES

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(Received April 24, 1984; in revised form June 25, 1984)

Summary

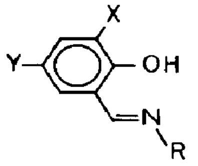
Unusually photosensitive Schiff bases were prepared from 3,5-di-*tert*-butylsalicylaldehyde and amines; the aniline derivative exhibits both normal and reverse photochromism on irradiation with UV light followed by either storage in the dark or irradiation with visible light. From a consistent kinetics explanation of the thermal back reaction, two courses for the photobleaching and the thermal fading of the photochromer, which is assigned to a quinoid amine form, are illustrated.

1. Introduction

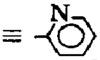
Interest in the photochromism and thermochromism of Schiff bases derived from salicylaldehyde and its derivatives has been maintained for three-quarters of a century [1, 2]; a number of publications on the phenomena have appeared especially in the last 2 decades. Although there is general agreement that the colouration processes involve an intramolecular proton transfer from the *o*-hydroxy group to the imine nitrogen atom followed by framework changes in the molecule [3 - 6], the structure of the coloured species is still the subject of intensive discussion. In the literature it has also been suggested that photochromism is associated with an open crystal structure which is composed of non-planar molecules, whereas thermochromism is associated with a close crystal structure which consists of planar molecules [7, 8]. In contrast with the active studies concerning the mechanistic interpretation of these phenomena, little effort has been directed towards designing molecules in such a way that the crystal habit can be controlled to give Schiff bases that are either photosensitive or thermosensitive as desired [5, 9]. There have been no clear directions to obtain photochromic crystals exclusively, since no correlation has been reported between photosensitivity and the chemical nature of ring substituents of *N*-salicylideneamines [10, 11].

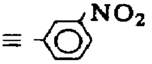
0047-2670/85/$3.30

It has been our view that introduction of bulky groups into the aromatic ring(s) of those compounds to increase the molecular breadth to allow partial framework movement in the crystal lattice is effective in producing photochromic crystals. For the first examples, we used 5-*tert*-butylsalicylaldehyde and 3,5-di-*tert*-butylsalicylaldehyde to prepare many photochromic Schiff bases satisfactorily. In this paper we report the unusual behaviour of the photosensitive Schiff bases



1: X ≡ H, Y ≡ H
2: X ≡ H, Y ≡ H, Y ≡ *tert*-butyl
3: X ≡ *tert*-butyl, Y ≡ *tert*-butyl

a: R ≡ Ph
b: R ≡ CH_2Ph
c: R ≡ $(CH_2)_2Ph$
d: R ≡ 

e: R ≡ 

and kinetics data of the resultant photochromers to gain a better understanding of the mechanism of the photochromism.

2. Experimental details

2.1. General comments

All melting points were taken in capillary tubes with a Shibata melting point apparatus. Proton nuclear magnetic resonance (NMR) spectra were determined on a Hitachi R-24 spectrometer by using $CDCl_3$ solutions with $(CH_3)_4Si$ as the internal standard. IR spectra were recorded in KBr disks on a Hitachi 295 IR spectrophotometer. Electronic spectra were measured with a Hitachi EPS-3T spectrophotometer. The elemental analyses were performed by the Service Centre for Elemental Analyses at Kyushu University.

2.2. Materials

5-*tert*-Butylsalicylaldehyde and 3,5-di-*tert*-butylsalicylaldehyde were prepared from the corresponding phenols under standard Reimer–Tiemann conditions [12, 13] and were identified by their boiling points and spectral data [13 - 15]. The Schiff bases used were prepared by direct condensation of the appropriate aldehyde with the appropriate amine in methanol or in ethanol, followed by repeated recrystallization in the dark to prevent any photoconversion by room light. All the products were identified by satisfactory elemental analytical data and spectral data to support the assignments and were stored in the dark. The Schiff bases derived from salicylaldehyde were known compounds [16], while the other Schiff bases were prepared in this study.

2.3. Product characterization data

The spectroscopic data for 2a (melting point, 92 - 93 °C) are as follows: IR (KBr), 1622 cm^{-1} (strong, C=N), 1585 cm^{-1} (strong, aromatic); NMR ($CDCl_3$), $\delta = 1.33$ ppm (singlet(s), 9 H, *tert*-butyl), $\delta = 6.85$ - 7.5 ppm (multiplet (m), 8 H, aromatic H), $\delta = 8.58$ ppm (s, 1 H, N=CH), $\delta = 12.98$ ppm (s, 1 H, OH). $C_{17}H_{19}NO$ requires 80.60% C, 7.56 % H and 5.53 % N. The results of analysis were as follows: 80.67% C, 7.63% H and 5.48% N.

The spectroscopic data for **2b** (melting point, 98 - 99 °C) are as follows: IR (KBr), 1636 cm^{-1} (strong, C=N), 1581 cm^{-1} (medium, aromatic); NMR ($CDCl_3$), $\delta = 1.28$ ppm (s, 9 H, *tert*-butyl), $\delta = 4.73$ ppm (s, 2 H, CH_2), $\delta = 6.88$ ppm (doublet (d), $J = 8.5$ Hz, 1 H, 3(H)), $\delta = 7.20$ ppm (d, $J = 2.5$ Hz, 1 H, 6(H)), $\delta = 7.26$ ppm (s, 5 H, aromatic H), $\delta = 7.32$ ppm (doublet of doublets, $J = 8.5$ Hz, $J = 2.5$ Hz, 1 H, 4(H)), $\delta = 8.37$ ppm (s, 1 H, N=CH), $\delta = 13.0$ ppm (broad singlet (bs), 1 H, OH). $C_{18}H_{21}NO$ requires 80.86% C, 7.92% H and 5.24% N. The results of analysis were as follows: 80.64% C, 7.93% H and 5.34% N.

The spectroscopic data for **2e** (melting point, 93 - 94 °C) are as follows: IR (KBr), 1625 cm^{-1} (medium, C=N), 1583 cm^{-1} (medium, aromatic), 1532 cm^{-1} (strong, NO_2), 1353 cm^{-1} (strong, NO_2); NMR ($CDCl_3$), $\delta = 1.31$ ppm (s, 9 H, *tert*-butyl), $\delta = 6.95$ ppm (d, $J = 8$ Hz, 1 H, 3(H)), $\delta = 7.39$ ppm (bs, 1 H, 6(H)), $\delta = 7.6 - 7.4$ ppm (m, 3 H, 4(H),4'(H),5'(H)), $\delta = 7.95 - 8.2$ ppm (m, 2 H, 2'(H),6'(H)), $\delta = 8.65$ ppm (s, 1 H, N=CH), $\delta = 12.3$ ppm (s, 1 H, OH). $C_{17}H_{18}N_2O_3$ requires 68.44% C, 6.08% H and 9.39% N. The results of analysis were as follows: 68.42% C, 6.16% H and 9.42% N.

The spectroscopic data for **3a** (melting point, 100 - 101 °C) are as follows: IR (KBr), 1618 cm^{-1} (strong, C=N), 1584 cm^{-1} (strong, aromatic); NMR ($CDCl_3$), $\delta = 1.35$ ppm (s, 9 H, *tert*-butyl), $\delta = 1.50$ ppm (s, 9 H, *tert*-butyl), $\delta = 7.15 - 7.5$ ppm (m, 7 H, aromatic H), $\delta = 8.60$ ppm (s, 1 H, N=CH), $\delta = 13.60$ ppm (s, 1 H, OH). $C_{21}H_{27}NO$ requires 81.51% C, 8.79% H and 4.53% N. The results of analysis were as follows: 81.36% C, 8.82% H and 4.56% N.

The spectroscopic data for **3b** (melting point, 93 - 95 °C) are as follows: IR (KBr), 1637 cm^{-1} (strong, C=N), 1599 cm^{-1} (weak, aromatic); NMR ($CDCl_3$), $\delta = 1.28$ ppm (s, 9 H, *tert*-butyl), $\delta = 1.42$ ppm (s, 9 H, *tert*-butyl), $\delta = 4.75$ ppm (s, 2 H, CH_2), $\delta = 7.05$ ppm (d, $J = 2.3$ Hz, 1 H, 6(H)), $\delta = 7.27$ ppm (s, 5 H, aromatic H), $\delta = 7.35$ ppm (d, $J = 2.3$ Hz, 1 H, 4(H)), $\delta = 8.40$ ppm (s, 1 H, N=CH), $\delta = 13.6$ ppm (bs, 1 H, OH). $C_{22}H_{29}NO$ requires 81.69% C, 9.04% H and 4.33% N. The results of analysis were as follows: 81.43% C, 9.15% H and 4.38% N.

The spectroscopic data for **3d** (melting point, 117 - 118 °C) are as follows: IR (KBr), 1614 cm^{-1} (medium, C=N), 1583 cm^{-1} (strong, aromatic), 1558 cm^{-1} (medium, aromatic); NMR ($CDCl_3$), $\delta = 1.32$ ppm (s, 9 H, *tert*-butyl), $\delta = 1.48$ ppm (s, 9 H, *tert*-butyl), $\delta = 7.25 - 7.05$ ppm (m, 2 H, 3'(H),5'(H)), $\delta = 7.33$ ppm (d, $J = 2.5$ Hz, 1 H, 6(H)), $\delta = 7.49$ ppm (d, $J = 2.5$ Hz, 1 H, 4(H)), $\delta = 7.75$ ppm (broad triplet, $J = 7$ Hz, 1 H, 4'(H)), $\delta = 8.48$ ppm (broad doublet, $J = 5$ Hz, 1 H, 6'(H)), $\delta = 9.44$ ppm (s, 1 H, N=CH), $\delta = 13.9$ ppm (s, 1 H, OH). $C_{20}H_{26}N_2O$ requires 77.38% C, 8.44% H and 9.02% N. The results of analysis were as follows: 77.14% C, 8.52% H and 8.98% N.

The spectroscopic data for **3e** (melting point, 132 - 133 °C) are as follows: IR (KBr), 1622 cm^{-1} (strong, C=N), 1590 cm^{-1} (strong, aromatic), 1522 cm^{-1} (strong, NO_2), 1357 cm^{-1} (strong, NO_2); NMR ($CDCl_3$), δ = 1.34 ppm (s, 9 H, *tert*-butyl), δ = 1.48 ppm (s, 9 H, *tert*-butyl), δ = 7.23 ppm (d, J = 2 Hz, 1 H, 6(H)), δ = 7.45 - 7.6 ppm (m, 3 H, 4(H),4'(H),-5'(H)), δ = 8.15 - 8.05 ppm (m, 2 H, 2'(H),6'(H)), δ = 8.67 ppm (s, 1 H, N=CH), δ = 13.1 ppm (s, 1 H, OH). $C_{21}H_{26}N_2O_3$ requires 71.16% C, 7.39% H and 7.90% N. The results of analysis were as follows: 70.94% C, 7.44% H and 7.99% N.

2.4. *Photocolouration and kinetics*

Crystalline powders of the Schiff bases were placed between two quartz plates and were stored in the dark overnight before the experiments were carried out. After their reflectance spectra had been measured in the initial state, photocolouration was achieved by irradiating the sample with 365 nm light; the reflectance spectra were then recorded at 25 °C at appropriate time intervals. The first-order rate constants k for the thermal fading reaction of the resultant photochromers were calculated from the variation in absorbance at around 480 nm with time using the expression

$$kt = \ln\left(\frac{A_0 - A_\infty}{A_t - A_\infty}\right)$$

where A_0, A_∞ and A_t are the observed absorbance data at zero time, at the end of the reaction (8 - 10 half-lives) and at time t (s) respectively. In the kinetics measurement for **3e**, the initial absorbance data before the photocolouration were used instead of A_∞ at the end of the thermal reaction because of the long half-life of **3e**.

In these measurements Al_2O_3 was used as a standard material and the sample was ground carefully on an agate mortar in the dark. Since the particle size was not controlled to be uniform it was not possible to ignore reabsorption [17]; thus, our results are qualitative only.

3. Results and discussion

The kinetics analysis of the thermal fading reaction of each photochromer exhibited a very good fit to a first-order equation. Some of the constructed first-order plots were not single straight lines but consisted of a two-stage transient decay (k_1 and k_2), showing the existence of two photocoloured species [10, 18].

As is apparent from Table 1, *tert*-butyl substituents increase the stability of the photoproduct in cases where methylene groups are not present between the nitrogen atom and the aromatic ring (**1a**, **2a**, **3a**). The effect of the bulky substituent is attributed to an increase in the open space for the molecular movement in the crystal lattice. Although crystalline **1e** and **2e** are

TABLE 1

Kinetics data for the thermal fading reaction of photochromers

Compound	k_1 (s^{-1})	k_2 (s^{-1})
1a	1.2×10^{-3}	8.3×10^{-5}
1b		3.1×10^{-4}
2a		7.8×10^{-5}
2b		7.7×10^{-4}
3a	1.0×10^{-3}	7.2×10^{-6}
3b		1.5×10^{-4}

not photochromic, **3e** produced an unusually stable photochromer ($k = 2.0 \times 10^{-7}$ s^{-1}). Its half-life (about 40 days) is by far the longest to date for this class of compounds, being 400 times that of unsubstituted **1a**. There must be enough room for the larger nitrophenyl group to change its position in the crystal lattice of **3e**.

In contrast, **3d** was not photochromic. The planarity of **3d** can be supposed on the basis of theoretical calculations and the X-ray crystal structure of **1d** [6, 8, 9]. Such a planar conformation arises from the long-range delocalization of π electrons and the loss of the electrostatic repulsion due to the contact of the azomethine proton and the *ortho* hydrogen of the aromatic ring when the aromatic CH moiety is replaced by a nitrogen atom [8]. This may be the reason for the high energy barrier in the photo-induced C=N bond rotation and the lack of photochromic activity of **3d**. Bulky substituents in such a pyridine derivative seem to be ineffective in producing photochromic crystals.

The rate constants for the Schiff bases derived from benzylamine (**1b**, **2b**, **3b**) were larger than those of the corresponding aniline derivatives (Table 1). From an inspection of molecular models, the flexible benzyl group is found to be preferable to the phenyl group for the molecular movement because of rotation around the C=N bond, although the benzyl group is larger in size than the phenyl group. Similar behaviour was found for **1c**, whose rate constants ($k_1 = 1.5 \times 10^{-2}$ s^{-1}, $k_2 = 1.9 \times 10^{-3}$ s^{-1}) were larger than those of **1b** and **1a**.

These facts suggest that the photochromic process involves a simple C=N bond rotation or a C=N bond rotation with a hybrid change at the nitrogen atom from sp^2 to sp^3. The former explanation is consistent with the photo-induced azomethine bond rotation of *N*-benzylideneaniline and its derivatives [19]. Thus, *o*-quinoid [5, 6, 11, 20, 21] and ion pair [22] forms resulting from rotation around the methine carbon–aromatic carbon bond are improbable structures for the photochromers, although such a rotation is still possible in a photoisomerization process. However, another *o*-quinoid form [23, 24] and a zwitterion [25] resulting from rotation around the azomethine bond have been shown to be the photochromer in other research papers.

In general, the colour of Schiff bases induced by UV light is photobleached on exposure to sunlight or artificial visible light [3, 18, 26]. Particular interest centres on 3a, which showed normal photochromism and photobleaching under the action of UV light and visible light respectively. However, after the photobleaching of the reddish orange colour of the photochromer to yellow by use of sunlight or a tungsten lamp, colour recovery in the dark was observed within 1 h ($k_3 = 2.0 \times 10^{-3}$ s^{-1}), after which time the resultant orange colour faded in the dark with time ($k = 6.9 \times 10^{-6}$ s^{-1}) to the yellow colour of the initial state. Although the thermal recolouration in the dark occurred in competition with some other thermal fading reaction, the cycle of the photobleaching and thermal colour-deepening process (reverse photochromism) could be repeated more than ten times (Fig. 1). These observations imply the existence of at least three stable photoisomers for this compound and of two different courses for the photobleaching and thermal fading of the photochromer.

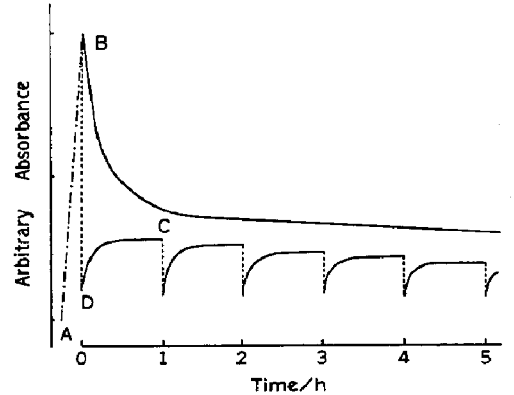
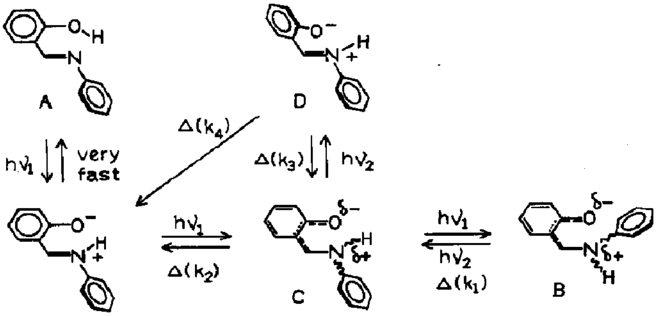


Fig. 1. Changes in 470 nm absorption of **3a** after irradiation with 365 nm light (— · —), exposure to sunlight (— — —) and storage in the dark (———).

In order to explain these results and the previously published data satisfactorily, one possible mechanism for the photoisomerization of *N*-salicylideneaniline can be shown schematically:



In the mechanism the nitrogen atoms of the photochromers are sp^3 hybridized and the π electron distribution in the molecule is considered to some extent. According to this model, observation of k_1 requires restricted rotation around the C—N bond, giving two rotamers B and C. This depends on the flexibility of the amine residue of the Schiff base. The reverse photochromism can be observed only when $k_3 \gtrsim k_4$. This depends on the balance between the mobility of the phenyl group of the benzylidene moiety and that of the amine residue of the Schiff base. Thus, by careful experiments 1b and 3e were found to exhibit similar reverse photochromism.

It is difficult to obtain direct evidence to support the mechanism of the photochromism. However, previously reported experimental results are consistent with this assignment of the photochromer. Recently, energy level diagrams of the photocolouration process of *N*-salicylideneaniline have been proposed in several papers [5, 11, 21], in which an *o*-quinoid form resulting from rotation around the methine carbon—aromatic carbon bond has been used for the structure of the photochromer. It should be noted that the questionable configuration of the photoproduct can be satisfactorily replaced by a configuration (B) proposed in this study.

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