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Crystalline photochromism of *N*-salicylidene-2,6-dialkylanilines: advantage of 2,6-dialkyl substituents of aniline for preparation of photochromic Schiff base crystals

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N-(3,5-Dihalosalicylidene)-2,6-dialkylaniline derivatives were prepared and their structure and photochromic properties were investigated. From the X-ray crystallography, it was revealed that steric repulsion between the azomethine hydrogen atom and the alkyl groups at the 2,6-positions of the aniline ring lead to a non-planar molecular structure, which was effective for the crystals to exhibit photochromism. The relationship between photochromicity and crystal packing of *N*-(3,5-dichlorosalicylidene)-2,6-dialkylanilines series was also discussed. The 2,6-dialkylaniline method was suggested to be applicable to the preparation of photochromic Schiff bases with various substituents in the salicylidene rings.

Introduction

Organic photochromic compounds have received considerable attention in recent years due to their potential applications such as optical data storage, electronic display system, optical switching devices, ophthalmic glasses, and so on.[1] Although photochromisms in solution or in dispersed states are well known, there are relatively few examples showing photochromism in the solid state which may provide actual accessibility for technical applications. *N*-Salicylideneaniline (Schiff base) is one of the typical compounds that exhibit photochromic phenomenon in the crystal state. Numerous studies on photochromic reactions of Schiff bases with various spectroscopic and theoretical approaches have presented a general agreement that the photochromic processes involve an intramolecular proton transfer from the *o*-hydroxy group to the imino nitrogen atom, followed by the framework alteration in the molecule (Fig. 1).[2] Crystallographic studies of some Schiff bases have also indicated topological problems and shown that molecular shape and array in the crystal lattice are crucial in exhibiting photochromism.[3] In contrast with extensive studies on mechanistic consideration of the phenomenon, little effort has been exerted to produce organic functional crystals that are photo-responsive and that control the crystal state properties. So far, we have already reported two effective methods for selective preparation of photochromic Schiff base crystals. One is the introduction of bulky *tert*-butyl groups into the salicylidene ring.[4] The *tert*-butyl substituent is suggested to act as a space-opener, which maintains room for the photo-induced molecular motion of Schiff base in the crystal. The other is the utilization of clathrate crystal lattice cavities of host deoxycholic acids, which provide the required room for photoisomerization of a guest Schiff base molecule.[5] Recently, we also prepared photochromic clathrate crystals of deoxycholamide and deoxycholyl alcohol as host molecules with Schiff bases as guests. It was shown that neighbouring molecular environment influenced strongly the photochromic properties of guest Schiff bases in the crystal lattice.[6] Now we provide the third effective method for yielding photosensitive Schiff bases by means of introduction of alkyl groups to the 2- and 6-positions of the aniline ring.

Bregman *et al.* has suggested that photochromism of Schiff bases is related to the conformation and packing of molecules in the crystal state.[3] Photochromic crystals are made up of non-planar molecules in which the aniline ring is significantly twisted out of the salicylidene moiety; thus, each molecule avoids tight packing force. As the molecules pack loosely, there is sufficient room for the photo-induced isomerization of the molecules to occur in the crystal lattice. As a consequence, to make molecules adopt a twisted conformation is a fundamental approach for the formation of photochromic Schiff base crystals. We will discuss steric repulsion between azomethine hydrogen atoms and alkyl substituents to lead to non-planar molecules that exhibit photochromism.

Results and discussion

N-Salicylideneaniline derivatives used in this study are shown in Scheme 1. These compounds were prepared by usual condensation of salicylaldehydes with anilines in alcohol and recrystallized from alcohol. We used 23 compounds for the investigation of solid state photochromism and structure determination, because the others were isolated as liquid at room temperature.

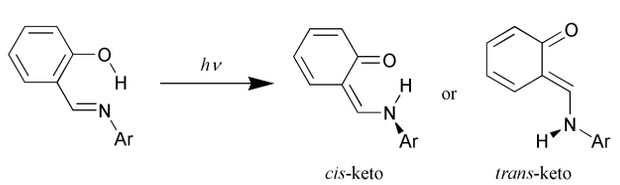
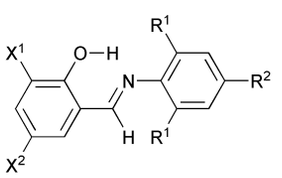


Fig. 1 Photochromic reaction of *N*-salicylideneanilines.



1: $X^1 = X^2 = Cl$
2: $X^1 = X^2 = Br$
3: $X^1 = X^2 = I$
4: $X^1 = X^2 = H$
5: $X^1 = X^2 = Bu^t$
6: $X^1 = H$, $X^2 = Cl$
7: $X^1 = H$, $X^2 = Br$

a: $R^1 = R^2 = H$
b: $R^1 = Me$, $R^2 = H$
c: $R^1 = Et$, $R^2 = H$
d: $R^1 = Pr^i$, $R^2 = H$
e: $R^1 = R^2 = Bu^t$

Scheme 1 *N*-Salicylideneanilines in this study.

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Table 1 Crystal data of **1a**

Data	**1a**
Formula	$C_{13}H_9Cl_2NO$
Formula weight	266.12
Crystal size/mm	0.3 × 0.1 × 0.1
Temperature/K	173
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	4.5249(2)
b/Å	19.1440(9)
c/Å	13.5302(4)
β	94.7150(10)°
V/Å^3	1168.08(8)
Z	4
D_{calc}/g cm^{-3}	1.513

Photosensitivity and structure of halosalicylidene Schiff bases without alkyl substituents in the aniline ring

From a preliminary survey of photo-sensitivities of aniline Schiff bases, halogen substituents in the salicylidene moiety were suggested to be effective to prepare non-photochromic crystals; thus, **1a**, **2a**, **3a**, **6a** and **7a** were not photochromic. In order to obtain structural information, we tried to examine their crystal structures. In the case of **1a**, careful crystallization from *n*-hexane yielded orange columns which were suitable for X-ray diffraction experiments to give a monoclinic crystal system of the space group of $P2_1/n$. The crystal data are listed in Table 1. Although the X-ray crystallographic analysis met with a difficulty for refinement due to some residual diffraction spots of the disordered molecule, it clearly revealed that two aromatic rings of **1a** were almost coplanar with a dihedral angle of 8.1°. The unimolecular structure in the crystal lattice and the packing diagram viewed along the *c* axis are shown in Figs. 2 and 3, respectively. The packing arrangement of **1a** is characteristic of flat molecules arranged in stacks along the *a* axis. Each molecule is inclined at about 45° to the *b* axis and is strongly held at an inter-planar distance of 3.3–3.5 Å in the manner of offset π–π stacking. Bregman *et al*. have reported the crystal and molecular structure of non-photochromic **6a** which adopts a planar structure similar to **1a**.[7] Such close parallel stacking would prevent any photo-induced isomerization, and accounts for the non-photochromic property of these crystals.

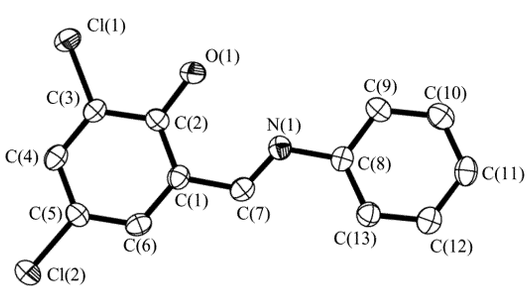

Fig. 2 An ORTEP drawing of **1a** with the numbering scheme. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are not drawn for clarity.

Photochromism of *N*-salicylidene-2,6-dialkylaniline crystals

The effect of alkyl groups at the 2- and 6-positions of the aniline ring of *N*-(3,5-dichlorosalicylidene)anilines on the photochromicity of the crystals was examined. Four analogues **1b**, **1c**, **1d** and **1e** were obtained as yellow crystals. From the hypochromic shifts compared to **1a**, whose colour was orange due to π-conjugation through the flat molecule, somewhat twisted molecular structure was postulated for these yellowish compounds. Photochromic properties of the *N*-(3,5-dichlorosalicylidene)-2,6-dialkylanilines crystals were then investigated. Contrary to our expectation, **1b** and **1e** did not show photochromism. Upon exposure of **1c** and **1d** to UV light, however, the yellowish colour of the crystals turned to orange, which returned slowly to the original yellow in the dark. The electronic spectra of **1d** before and after UV irradiation are shown in Fig. 4. The fact that photochromic phenomenon appeared for **1c** and **1d** with alkyl substituents suggests a possible way for crystal engineering to construct photochromic Schiff base systems.

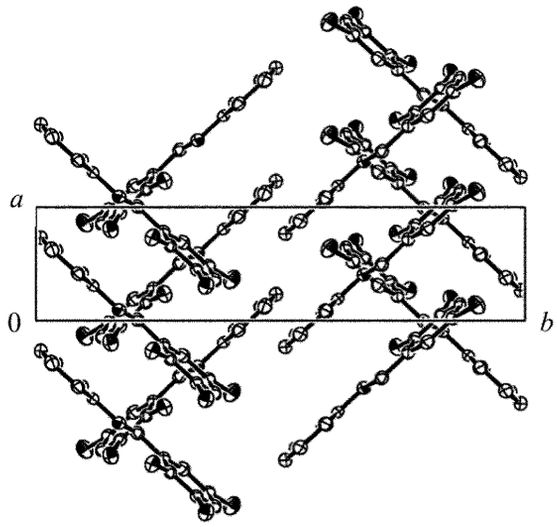

Fig. 3 Packing diagram along the *c* axis of **1a**.

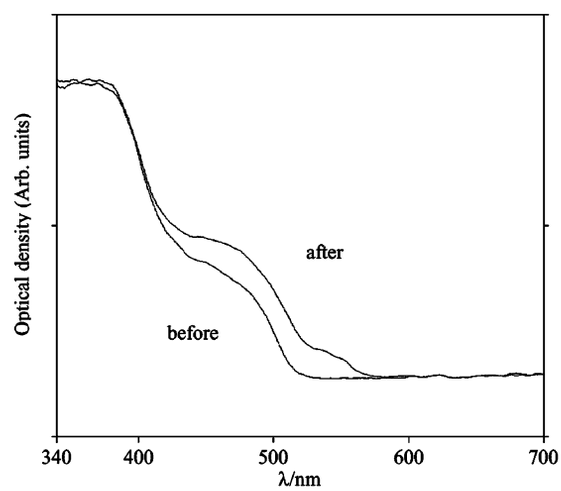

Fig. 4 Solid state reflectance spectra of **1d** before and after UV irradiation.

In order to confirm the effectiveness of the 2,6-dialkyl substitutions for preparation of photochromic Schiff bases, we extended our discussion to photo-sensitivities of other *N*-salicylidene-2,6-dialkylaniline derivatives. The obtained crystals of 2,6-dialkylaniline derivatives of halogen-possessing compounds **2**, **3**, **6** and **7** as well as ones derived from the series of **4** and **5** were found to be mostly photochromic (Table 2). These results show that the introduction of alkyl groups to the 2,6-positions of the aniline ring is an effective method for preparation of photochromic *N*-salicylideneanilines. For certain reasons, some of the desired compounds were isolated as liquid. In such a case the introduced alkyl substituents might disturb the construction of crystals in which molecules must arrange close together. Particularly, 2,6-diethylaniline derivatives **c** were rather intractable compounds; they were apt to be isolated as yellow oil or as fine powder with low melting point when they solidified. This is presumably due to the conformational flexibility of the ethyl group. On the other hand, methyl and isopropyl

Table 2 Photochromicities of *N*-salicylideneaniline crystals

	1	2	3	4	5	6	7
a	No	No	No	Yes	Yes	No	No
b	No	No	No	—	Yes	—	Yes
c	Yes	Yes	Yes	—	—	—	—
d	Yes	Yes	Yes	Yes	Yes	Yes	Yes
e	No	—[a]	—	—	—	—	—

[a] Denotes that this compound cannot be isolated as crystals.

groups are preferential substituents to form crystals. For yielding photochromic Schiff base crystals it is important to choose suitable substituents that provide both appropriate torsion of the molecule and also interspaces for isomerization motions in the crystal. These observations present an important guideline for facile isolation of photochromic Schiff base crystals.

Since all *N*-salicylidene-2,6-diisopropylaniline derivatives in this study were isolated as photochromic crystals, isopropyl group was suggested to be the most useful substituent for preparation of photochromic Schiff base crystals.

Relationship between photochromicity and crystal packing for *N*-salicylidene-2,6-dialkylaniline derivatives

X-Ray crystallographic analyses of some *N*-(3,5-dichlorosalicylidene)-2,6-dialkylanilines were carried out in order to gain information on how the molecular structure of the Schiff base could change by the introduction of alkyl groups at the 2,6-positions of the aniline ring of **1a**, which adopts a planar structure. Recrystallization of **1b**, **1d** and **1e** from methanol yielded single crystals suitable for X-ray diffraction measurements. They crystallized in the monoclinic crystal system with space group $P2_1/c$ for **1b** and $P2_1/n$ for **1d** and **1e**. The crystal data are listed in Table 3. The molecular structures of **1b**, **1d** and **1e** are presented in Fig. 5. In the case of **1d**, whose structure has been reported at 110 K,[8] there were two crystallographically independent molecules in the unit cell. The most significant feature was the observation that the aniline rings of these compounds were clearly twisted out of the salicylidene planes in the crystal state due to the steric requirements of the alkyl groups.

Table 3 Crystal data of **1b**, **1d** and **1e**

Data	**1b**	**1d**	**1e**
Formula	$C_{15}H_{13}Cl_2NO$	$C_{19}H_{21}Cl_2NO$	$C_{25}H_{33}Cl_2NO$
Formula weight	294.17	350.28	434.45
Crystal size/mm	0.5 × 0.3 × 0.2	0.4 × 0.3 × 0.2	0.2 × 0.15 × 0.1
Temperature/K	296	296	293
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$
a/Å	12.7170(10)	11.253(3)	13.8050(4)
b/Å	9.179(3)	14.858(3)	11.6390(3)
c/Å	13.527(2)	22.726(3)	15.6289(4)
β	116.965(9)°	91.096(17)°	97.0510(10)°
V/Å^3	1407.3(4)	3799.0(13)	2492.20(12)
Z	4	8	4
D_{calc}/g cm^{-3}	1.388	1.225	1.158

The dihedral angles between the least-square's planes defined by the salicylidene rings and the aniline rings were 63.5° for **1b**, 82.3° and 73.6° for **1d** and 82.9° for **1e**, respectively. More bulky alkyl groups are prone to increase the degree of twisting of the molecules. It can therefore be presumed that **1c**, whose crystal structure could not be elucidated, adopts a twisted structure with a dihedral angle in between 64° and 75°.

The remaining problem is the elucidation of reasons why compounds **1b** and **1e** are not photochromic. Since the degree of twisting of the molecules could not give any logical explanation for the non-photochromicity of **1b** and **1e**, molecular arrangements could be associated with photophysical properties of crystals. Therefore their crystal packings were examined in detail. The packing diagrams and side views of the centrosymmetric dimers of **1b** and **1e** are shown in Figs. 6 and 7, respectively. The packing structure demonstrates that the crystal of **1b** is built up from a columnar unit wherein centrosymmetric dimers line up along the *a* axis. The salicylidene rings of opposite molecules are located cofacially in offset stacking of the dimer. The Cl(1) ··· C(2*) distance is 3.590 Å, where * designates a symmetry operation of $(-x, -y, -z)$ and the distance from the least-squares plane defined by the six atoms C(8)–C(9)–C(11)–C(12)–C(13)–C(14) in the aniline ring to neighbouring C(15**) of methyl group is 3.615 Å, where **

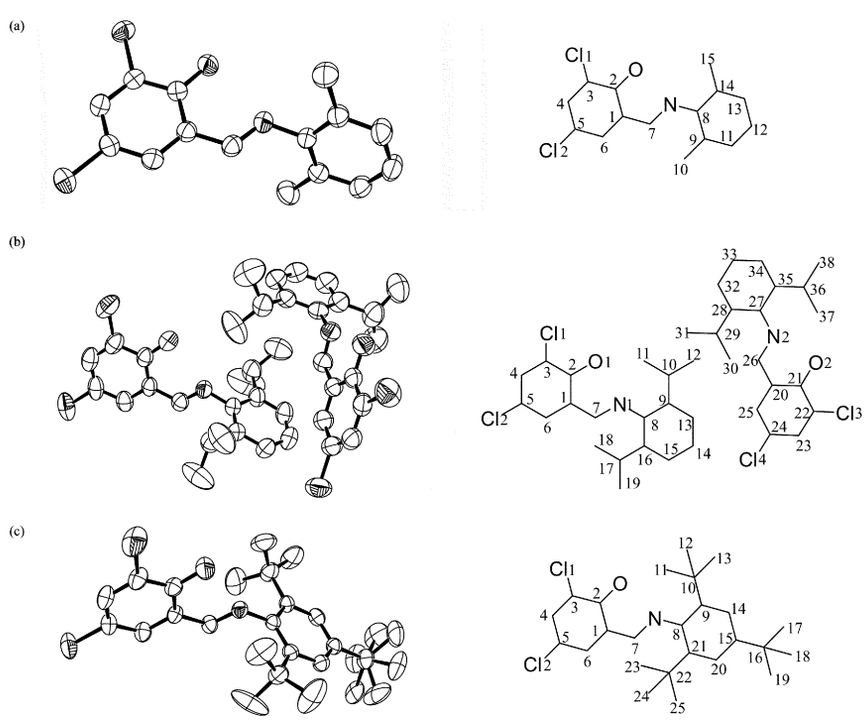

Fig. 5 ORTEP drawings of **1b** (a), **1d** (b) and **1e** (c). Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are not drawn for clarity. The schematic drawings of each asymmetric unit are shown on the right side of the ORTEP drawings with the numbering scheme.

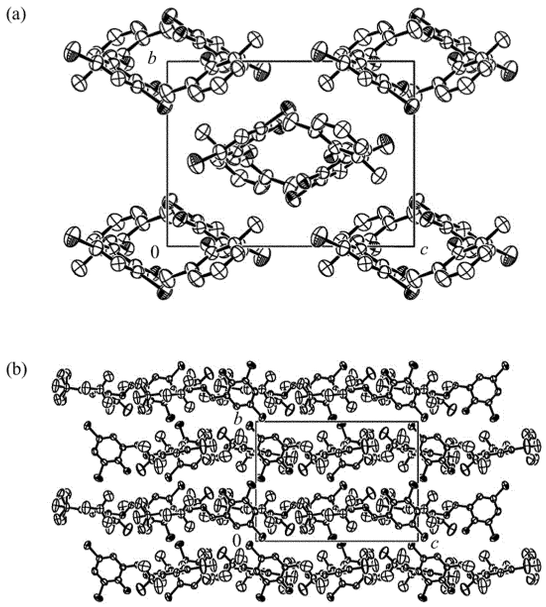

Fig. 6 Packing diagrams of **1b** (a) and **1e** (b) along the *a* axis.

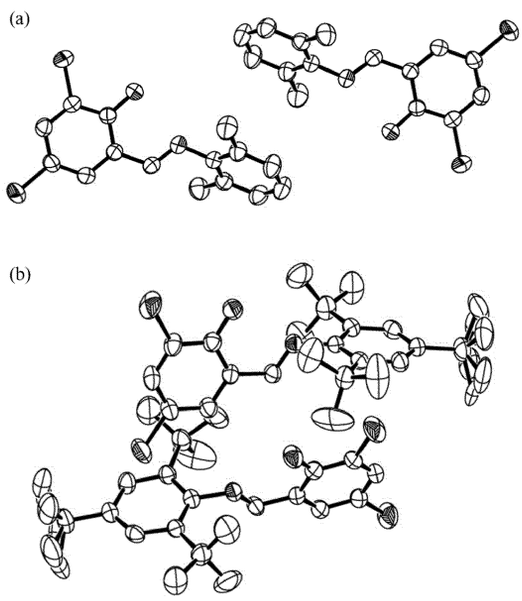

Fig. 7 Centrosymmetric dimers of **1b** (a) and **1e** (b).

indicates a symmetry operation of $(-1-x, -y, -z)$. These observations indicate that the methyl group is situated on the adjoining aminoaromatic ring within van der Waals contact. The columnar unit is arranged in a "bricks in a wall" fashion. The distance between O(1) and C(10***) of another methyl group is 3.204 Å, which is smaller than the sum of van der Waals radii of oxygen atoms (1.52 Å)[9] and methyl group (2.0 Å),[10] where *** designates a symmetry operation of $(+x, \frac{1}{2} - y, -\frac{1}{2} + z)$. The methyl group is situated in the cleft among columns and regarded as "cement united bricks".

In the case of **1e**, the aniline ring is almost perpendicular to the plane of the salicylidene moiety because of the bulkiness of the two *tert*-butyl groups at the 2,6-positions. The photoisomerization reaction site of the molecule is very crowded. In the crystal lattice the molecules are arranged in a head-to-tail fashion oriented along the *c* axis. The 1-D chain is associated with an antiparallel chain to form 2-D sheet on the *bc* plane, where two chlorine atoms are situated in the neighbouring concave part at the aniline moiety on both sides in the edge-on manner. The 2-D sheets are laminated to build up the 3-D crystal structure, in which *tert*-butyl groups are involved in each sheet. As for the crystals in which some parts of the molecules get entangled with each other, any types of photo-induced molecular motion would be hampered. The tightly packed crystal structure would result in non-photochromic property of such a Schiff base.

In the crystal lattice of **1d**, on the other hand, two crystallographically independent molecules form a bent dimeric motif (Fig. 5(b)). A molecule pairs up with the opposite one to make a columnar cluster, which is oriented down to the *a* axis. The isopropyl groups are directed toward the pillar hole in the column and located in a V-shaped groove outside the column (Fig. 8). The adequate size and shape of the isopropyl group disturbs the intermolecular close contacts and weakens the molecular interactions, resulting favourably in occurrence of photochromic character of these Schiff bases.

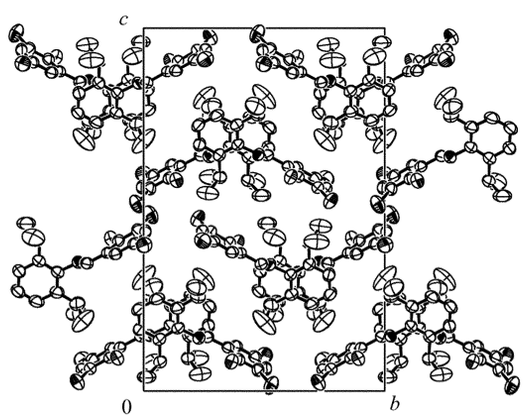

Fig. 8 Packing diagram of **1d** along the *a* axis.

Conclusion

Crystals of 23 Schiff bases were prepared mainly from 5-halosalicylaldehydes or 3,5-dihalosalicylaldehydes and 2,6-dialkylanilines: their photochromic properties and crystal structures were investigated. Most *N*-salicylidene-2,6-dialkylanilines exhibited photochromism in the crystal state. Thus, the employment of 2,6-dialkylanilines was found to be a useful and widely applicable method for preparation of photochromic Schiff base crystals. The alkyl substituents in the aniline ring were suggested to act as space openers that can weaken the molecular packing force in the crystal lattice and make the crystals photochromic. It is concluded that 2,6-diisopropylaniline is the most practical material to prepare photochromic Schiff bases which can possess various kinds of substituents in the salicylidene ring.

Experimental

General comments

Elemental analyses were performed by the Service Center of the Elementary Analysis of Organic Compounds affiliated to the Faculty of Science in Kyushu University. ^{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).

Preparation of *N*-salicylideneanilines

Starting salicylaldehydes and anilines were commercially available and were used without further purification. Each Schiff base studied was prepared by standard condensation of 2 mmol of the corresponding salicylaldehyde and aniline in methanol. The resulting crude product was collected by suction filtration and recrystallized from methanol to yield pure compound. Compounds **4b**, **4c**, **5c**, **6b**, **6c** and **7c** were obtained as liquid at room temperature. These were not employed for further investigation. Melting points of **1a**,[11] **1b**,[12] **1d**,[8] **2a**,[11] **3a**,[13] **4d**,[14] **5a**,[4]

5b,[15] **5d**,[16] **6a**[17] and **7a**[17] were the same as reported in the literature. Characterizations of new compounds are described below.

N-(3,5-Dichlorosalicylidene)-2,6-diethylaniline (1c)

Yield: 613 mg (95.1%), mp: 68.0–68.5 °C (Found: C, 63.24; H, 5.36; N, 4.37. $C_{17}H_{17}Cl_2NO$ requires C, 63.37; H, 5.32; N, 4.35%); δ_H(270 MHz; $CDCl_3$): 1.15 (6 H, t, CH_3CH_2), 2.53 (4 H, q, CH_3CH_2), 7.15 (3 H, br s, 3(H), 4(H), 5(H)), 7.26 (1 H, d, *J* 3, 6′(H)), 7.51 (1 H, d, *J* 3, 4′(H)), 8.28 (1 H, s, CH=N), 13.94 (1 H, br s, OH).

N-(3,5-Dichlorosalicylidene)-2,4,6-tri-*tert*-butylaniline (1e)

Yield: 400 mg (46.0%), mp: 185.5–186.5 °C (Found: C, 69.26; H, 7.66; N, 3.22. $C_{25}H_{33}Cl_2NO$ requires C, 69.12; H, 7.66; N, 3.22%); δ_H(270 MHz; $CDCl_3$): 1.32 (18 H, s, 2,6-Bu^t), 1.34 (9 H, s, 4-Bu^t), 7.17 (1 H, d, *J* 2, 6′(H)), 7.40 (2 H, br s, 3(H), 5(H)), 7.51 (1 H, d, *J* 2, 4′(H)), 8.15 (1 H, s, CH=N), 14.22 (1 H, br s, OH).

N-(3,5-Dibromosalicylidene)-2,6-dimethylaniline (2b)

Yield: 608 mg (79.3%), mp: 107.5–108.0 °C (Found: C, 47.01; H, 3.33; N, 3.62. $C_{15}H_{13}Br_2NO$ requires C, 47.03; H, 3.42; N, 3.66%); δ_H (270 MHz; $CDCl_3$): 2.20 (6 H, s, CH_3), 7.03–7.14 (3 H, m, 3(H), 4(H), 5(H)), 7.43 (1 H, d, *J* 2, 6′(H)), 7.79 (1 H, d, *J* 2, 4′(H)), 8.25 (1 H, s, CH=N), 14.14 (1 H, br s, OH).

N-(3,5-Dibromosalicylidene)-2,6-diethylaniline (2c)

Yield: 408 mg (50.0%), mp: 75.0–75.5 °C (Found: C, 49.69; H, 4.17; N, 3.38. $C_{17}H_{17}Br_2NO$ requires C, 49.66; H, 4.17; N, 3.41%); δ_H(270 MHz; $CDCl_3$): 1.15 (6 H, t, CH_3CH_2), 2.52 (4 H, q, CH_3CH_2), 7.14 (3 H, br s, 3(H), 4(H), 5(H)), 7.43 (1 H, d, *J* 2, 6′(H)), 7.79 (1 H, d, *J* 2, 4′(H)), 8.24 (1 H, s, CH=N), 14.07 (1 H, br s, OH).

N-(3,5-Dibromosalicylidene)-2,6-diisopropylaniline (2d)

Yield: 604 mg (69.4%), mp: 118.0–119.0 °C (Found: C, 51.90; H, 4.81; N, 3.16. $C_{19}H_{21}Br_2NO$ requires C, 51.96; H, 4.80; N, 3.19%); δ_H(270 MHz; $CDCl_3$): 1.18 (12 H, d, $(CH_3)_2CH$), 2.92 (2 H, sept, $(CH_3)_2CH$), 7.20 (3 H, br s, 3(H), 4(H), 5(H)), 7.44 (1 H, d, *J* 2, 6′(H)), 7.80 (1 H, d, *J* 2, 4′(H)), 8.20 (1 H, s, CH=N), 14.15 (1 H, br s, OH).

N-(3,5-Diiodosalicylidene)-2,6-dimethylaniline (3b)

Yield: 878 mg (91.8%), mp 161.0–162.0 °C (Found: C, 37.51; H, 2.68; N, 2.86. $C_{15}H_{13}I_2NO$ requires C, 37.76; H, 2.75; N, 2.94%); δ_H(270 MHz; $CDCl_3$): 2.19 (6 H, s, Me), 7.04–7.13 (3 H, m, 3(H), 4(H), 5(H)), 7.60 (1 H, d, *J* 2, 6′(H)), 8.13 (1 H, d, *J* 2, 4′(H)), 8.15 (1 H, s, CH=N), 14.33 (1 H, br s, OH).

N-(3,5-Diiodosalicylidene)-2,6-diethylaniline (3c)

Yield: 943 mg (93.2%), mp 112.5–113.5 °C (Found: C, 40.40; H, 3.35; N, 2.78. $C_{17}H_{17}I_2NO$ requires C, 40.42; H, 3.39; N, 2.77%); δ_H(270 MHz; $CDCl_3$): 1.14 (6 H, t, CH_3CH_2), 2.51 (4 H, q, CH_3CH_2), 7.14 (3 H, br s, 3(H), 4(H), 5(H)), 7.60 (1 H, d, *J* 2, 6′(H)), 8.14 (1 H, d, *J* 2, 4′(H)), 8.15 (1 H, s, CH=N), 14.27 (1 H, br s, OH).

N-(3,5-Diiodosalicylidene)-2,6-diisopropylaniline (3d)

Yield: 932 mg (87.5%), mp 130.0–131.5 °C (Found: C, 42.83; H, 3.95; N, 2.65. $C_{19}H_{21}I_2NO$ requires C, 42.80; H, 3.97; N, 2.63%); δ_H(270 MHz; $CDCl_3$): 1.17 (12 H, d, $(CH_3)_2CH$), 2.91 (2 H, sept, $(CH_3)_2CH$), 7.20 (3 H, br s, 3(H), 4(H), 5(H)), 7.61 (1 H, d, *J* 2, 6′(H)), 8.10 (1 H, s, CH=N), 8.15 (1 H, d, *J* 2, 4′(H)), 14.29 (1 H, br s, OH).

N-(5-Chlorosalicylidene)-2,6-diisopropylaniline (6d)

Yield: 499 mg (79.1%), mp 112.5–114.0 °C (Found: C, 72.19; H, 7.01; N, 4.49. $C_{19}H_{22}ClNO$ requires C, 72.25; H, 7.02; N, 4.43%); δ_H(270 MHz; $CDCl_3$): 1.31 (12 H, d, $(CH_3)_2CH$), 2.91 (2 H, sept, $(CH_3)_2CH$), 6.97 (1 H, d, *J* 9, 3′(H)), 7.15 (3 H, br s, 3(H), 4(H), 5(H)), 7.27 (1 H, d, *J* 2, 6′(H)), 7.31 (1 H, dd, *J* 9 and 2, 4′(H)), 8.19 (1 H, s, CH=N), 13.03 (1 H, br s, OH).

N-(5-Bromosalicylidene)-2,6-dimethylaniline (7b)

Yield: 532 mg (87.6%), mp 77.5–78.0 °C (Found: C, 59.14; H, 4.65; N, 4.57. $C_{15}H_{14}BrNO$ requires C, 59.23; H, 4.64; N, 4.60%); δ_H(270 MHz; $CDCl_3$): 2.19 (6 H, s, Me), 6.94–7.12 (4 H, m, 3(H), 4(H), 5(H), 3′(H)), 7.44–7.50 (2 H, m, 4′(H), 6′(H)), 8.27 (1 H, s, CH=N), 13.09 (1 H, br s, OH).

N-(5-Bromosalicylidene)-2,6-diisopropylaniline (7d)

Yield: 552 mg (79.0%), mp 113.5–115.0 °C (Found: C, 63.26; H, 6.15; N, 3.86. $C_{19}H_{22}BrNO$ requires C, 63.34; H, 6.15; N, 3.89%); δ_H(270 MHz; $CDCl_3$): 1.18 (12 H, d, $(CH_3)_2CH$), 2.95 (2 H, sept, $(CH_3)_2CH$), 6.97 (1 H, dd, *J* 9 and 1, 3′(H)), 7.19 (3 H, d, *J* 1, 3(H), 4(H), 5(H)), 7.46–7.51 (1 H, m, 4′(H), 6′(H)), 8.23 (1 H, s, CH=N), 13.11 (1 H, br s, OH).

Photocolouration 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. Photocolouration was accomplished by irradiating the sample with 365 nm UV-A 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 *n*-hexane (**1a**) or methanol (others). Each crystal was mounted at the end of a glass fiber and coated with epoxy resin. For **1b** and **1d**, X-ray diffraction experiments were performed on a Rigaku AFC7R X-ray diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å) and a rotating anode generator. For **1a** and **1e**, X-ray diffraction experiments were carried out on a Rigaku RAXIS-IV imaging plate area detector with graphite monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å). Brief summaries of crystal data are given in Tables 1 and 3. Data analyses were carried out with the CrystalStructure™ crystallographic software package.[18] The structure was solved by direct methods using SHELXS-97[19] and refined by full matrix least-squares on F^2 with SHELXL-97.[19] The non-hydrogen atoms were refined anisotropically. Some hydrogen atoms were refined isotropically, the rests were fixed geometrically and not refined. The plots of the molecules were obtained by ORTEP3[20] included in the WinGX software.[21]

N-(3,5-Dichlorosalicylidene)aniline (1a)

Of the 9823 reflections which were collected, 2616 were independent ($R_{int} = 0.0369$); equivalent reflections were merged. The linear absorption coefficient, μ, for Mo-Kα radiation is 0.535 mm^{-1}. An extinction coefficient was refined to 0.012(4). The structure was refined on F^2 with 155 parameters to R_1 0.1114, wR_2 0.3262 for 2616 reflections with $I > 2\sigma(I)$ and R_1 0.1216, wR_2 0.3366 for all data. The highest residual peak was located near to salicylidene ring (1.83 and 1.76 eÅ^{-3}) assigned

† CCDC reference numbers 200498–200501. See http://www.rsc.org/suppdata/ob/b2/b212295b/ for crystallographic data in .cif or other electronic format.

as chlorine atom of disordered minor component which could not be optimised.

N-(3,5-Dichlorosalicylidene)-2,6-dimethylaniline (1b)

Of the 3370 reflections which were collected, 3233 were independent (R_{int} = 0.0358). The linear absorption coefficient, μ, for Mo-Kα radiation is 0.452 mm^{-1}. An extinction coefficient was refined to 0.0023(13). The structure was refined on F^2 with 225 parameters to R_1 0.0344, wR_2 0.0965 for 3233 reflections with $I > 2\sigma(I)$ and R_1 0.0493, wR_2 0.1056 for all data.

N-(3,5-Dichlorosalicylidene)-2,6-diisopropylaniline (1d)

Of the 7045 reflections which were collected, 6682 were independent (R_{int} = 0.0611); equivalent reflections were merged. The linear absorption coefficient, μ, for Mo-Kα radiation is 0.345 mm^{-1}. An extinction coefficient was refined to 0.0014(4). The structure was refined on F^2 with 488 parameters to R_1 0.0458, wR_2 0.1324 for 6682 reflections with $I > 2\sigma(I)$ and R_1 0.1126, wR_2 0.1617 for all data.

N-(3,5-Dichlorosalicylidene)-2,4,6-tri-*tert*-butylaniline (1e)

Of the 22697 reflections which were collected, 5711 were independent (R_{int} = 0.1178); equivalent reflections were merged. The linear absorption coefficient, μ, for Mo-Kα radiation is 0.275 mm^{-1}. An extinction coefficient was refined to 0.0034(9). The structure was refined on F^2 with 355 parameters to R_1 0.0885, wR_2 0.1714 for 5711 reflections with $I > 2\sigma(I)$ and R_1 0.1714, wR_2 0.2131 for all data. The *tert*-butyl group at the 4-position in the aniline ring was found to be disordered. Two orientations of carbon atoms were included in the model with occupancies of 0.85 and 0.15.

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