The α_2-polymorph of salicylidene-aniline[1]

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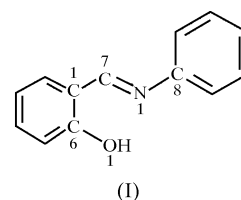Correspondence e-mail: frederic.arod@epfl.ch

N-Salicylideneaniline (SA), $C_{13}H_{11}NO$, belongs to the large family of aromatic Schiff bases. It is of particular importance owing to its reversible photoreactivity. SA forms two photochromic polymorphs, both with two non-coplanar benzene rings. In addition, we have recently discovered a planar polymorph, named the β-polymorph, which will be discussed in a subsequent paper. We report here the structure of the α_2-polymorph in the orthorhombic crystal system. This compound exhibits a strong intramolecular O—H···N hydrogen bond and the dihedral angle between the two rings varies with temperature.

Comment

Photochromism of aromatic molecules has been known and discussed for a long time (Senier & Shepheard, 1909; Senier et al., 1912). Schiff bases are important in diverse fields of chemistry and biochemistry owing to their biological activity (Lozier et al., 1975; Garnovskii et al., 1993) and can be classified according to their photochromic or thermochromic properties (Cohen et al., 1964; Hadjoudis et al., 1987). Some anils of salicylaldehyde have attracted the interest of chemists and physicists because of their reversible photoreactivity in the solid state. The design and synthesis of organic compounds with specific physical properties via crystal engineering is under development.

Aromatic Schiff bases are a typical class of photochromic materials, involving both ESIPT (excited state intramolecular proton transfer) and cis–trans isomerization to form an orange–red photoproduct from the colourless crystal. It is generally accepted that the stable form of the molecule of N-salicylideneaniline (SA), (I), in the ground state is a pale-yellow trans-enol isomer with an intramolecular hydrogen bond between the hydroxyl group and the N atom. Upon photoexcitation with ultraviolet (UV) light, this form undergoes an ultrafast H-atom transfer from the hydroxyl group to the N atom. Because of an electronic redistribution in the excited state, the two benzene rings rotate around the C7—N axis. A coloured species (dark orange), the keto form, is then produced in the excited singlet state. However, the details of the structural configuration of the keto form give rise to competition between forms in which the O atom and the imine H atom will be in cis or trans configurations with regard to the C7—N bond (Hadjoudis, 1995; Shen et al., 2000). The coloured species can be reversibly bleached, either by irradiation using visible light or upon heating the crystals. The photochromic reaction of SA has been extensively studied using various spectroscopic methods (Otsubo et al., 2002, and references therein).

(I)

In 1964, Cohen et al. observed the polymorphism of anils and also determined the space group and lattice constants of (I), which are consistent with the corresponding values presented here. We report for the first time the complete structure of the α_2-polymorph of SA in the ground state (Fig. 1). We selected a small crystal in order to perform spectroscopic measurements as well.

Some of the distances and angles of (I) are very different from the values given by Destro et al. (1978) for the α_1-polymorph, where some distances and angles were themselves judged to be out of the expected range. For example, the C6—O or C1—C7 distances of 1.320 (7) and 1.529 (5) Å for the α_1-polymorph are very different from our values for the α_2-polymorph of 1.353 (3) and 1.450 (3) Å at room temperature and 1.352 (3) and 1.455 (3) Å at low temperature. Moreover, all the angles previously mentioned by Destro et al. (1978) as being out of the expected range exhibit satisfactory values in the present model.

The bond lengths and angles of (I) are in agreement with the values given in *International Tables for Crystallography* (Allen et al., 1999). Some of these values will now be discussed in more detail by comparison with similar compounds
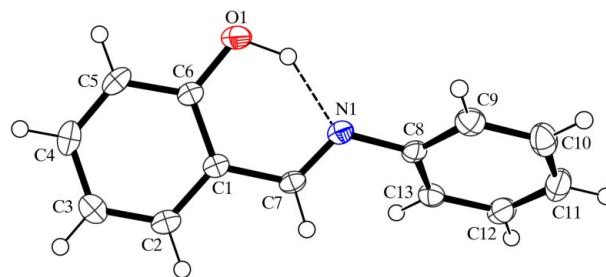

Figure 1
The molecular structure of (I), showing the atom-numbering scheme and the intramolecular hydrogen bonding (dashed line). Displacement ellipsoids are plotted at the 50% probability level.

(Bregman, Leiserowitz & Osaki, 1964; Bregman, Leiserowitz & Schmidt, 1964; Burr & Hobson, 1969; Destro *et al.*, 1978; Lindeman *et al.*, 1982*a,b*; Elmali & Elerman, 1997, 1998; Elmali *et al.*, 1998; Burgess *et al.*, 1999; Harada *et al.*, 1999; Fukuda *et al.*, 2003; Karadayı *et al.*, 2003; Yeap *et al.*, 2003).

Lindeman *et al.* (1982*a,b*) suggested that the two compounds *N*-salicylidene-4-chloroaniline (planar) and *N*-salicylidene-4-bromoaniline (non-planar) differ only in their conformation, while the other geometric parameters are close to each other. On the other hand, Ogawa *et al.* (1998) reported that the lengths of each of those bonds which can change by tautomerism, specifically C1—C6, C1—C7, C6—O and C7—N, are significantly different between the OH and NH forms.

The heteroatom bonds are those most affected by molecular self-isomerization (H-atom transfer). The C6—O bond is the most sensitive indicator of the type of tautomeric form. This is a single bond for the enol–imino tautomers, comparable with those in phenols [1.362 (15) Å], while it is shortened in the keto–amino tautomers. These values lie between those found in phenols and benzoquinones [1.222 (13) Å]. In contrast, the C7—N bond is lengthened to 1.339 (16) Å in the keto tautomer, while in the enol tautomer it is 1.279 (8) Å. The C6—O and C7—N bond distances of the α_2-polymorph are 1.352 (3) and 1.281 (3) Å, respectively, and correspond to the enol isomer, in agreement with the expected ground-state conformation.

The wide range of the C7=N bond lengths has been the subject of many discussions, and several hypotheses have been invoked to explain the apparent shortening at room temperature (Bregman, Leiserowitz & Osaki, 1964; Moustakali-Mavridis *et al.*, 1978; Harada *et al.*, 2004). A torsional vibration of the C—Ph and N—Ph bonds, resulting in a temperature dependence of the C7=N bond length, has been postulated in analogy with benzylideneanilines, (*E*)-stilbenes, azobenzenes and 1,2-diphenylethanes (Ogawa *et al.*, 1992, 1995; Harada *et al.*, 1995, 1997, 2004; Harada & Ogawa, 2001). In the α_2-polymorph, we also observe a decrease in the C7=N bond length, from 1.281 (3) to 1.267 (3) Å, with increasing temperature from 120 to 293 K, but librational shortening is improbable since the largest displacement component is along the bond. The other bond lengths (*e.g.* C1—C7 and N1—C8) change little with temperature, which prevents the use of Schomaker & Trueblood's rigid-body model (Schomaker & Trueblood, 1968). The thermal displacements are approximately proportional to the temperature. A possible asphericity shift of the atomic positions due to the bonding electrons is then expected to be temperature independent and cannot explain the shortening of the bond.

Fig. 2 shows a difference electron-density map at 120 K, revealing the position of the H atom. The map clearly shows a peak that can be assigned to one H atom connected to atom O1. The H atom belonging to the oxygen site was found at an O1—H1*A* distance of 1.02 (4) Å and the C6—O1—H1*A* bond angle is 109 (2)°, as expected. A strong intramolecular hydrogen bond (O—H⋯N) occurs between atoms O1 and N1 [2.615 (3) Å], the H being bonded to atom O1. This

distance is significantly shorter than the sum of the van der Waals radii for N and O (3.07 Å; Bondi, 1964) and is comparable with those observed for other similar compounds. We have also discovered a planar polymorph the study of which will be published elsewhere. The β-polymorph is thermochromic and it crystallizes in space group $Pbc2_1$; the unit cell at 120 K is: $a = 5.7918$ (6) Å, $b = 13.6449$ (15) Å and $c = 13.6449$ (15) Å.

Since the same compound may occur in dimorphs, of which one is thermochromic and the others are photochromic, it seems that it is the crystal structure which determines this behaviour, rather than the molecule as such. From observations on some thermochromic and photochromic Schiff base compounds, it was proposed that molecules exhibiting thermochromism are planar, while those exhibiting photochromism are non-planar (Moustakali-Mavridis *et al.*, 1978). Bregman, Leiserowitz & Osaki (1964) have suggested that photochromism of Schiff bases is related to the conformation and packing of molecules in the crystal state. 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 forces. As the molecules pack loosely, there is sufficient room for the photo-induced isomerization of the molecules to occur in the crystal lattice.

The most striking feature in (I) is the twist of the aniline ring out of the C1—C7=N1—C8 plane by 47.3° at 120 K, compared with 45.1° at room temperature. The twist of the benzylidene ring out of this plane is much smaller (7.1° at 120 K to 6.6° at room temperature). The angle between the two benzene rings in the α_2-polymorph is 54.1° at 120 K, compared with 51.4° at room temperature. In the α_1 form, Destro *et al.* (1978) reported 49°. Only two other cases relating to this study were found. However, they concern planar
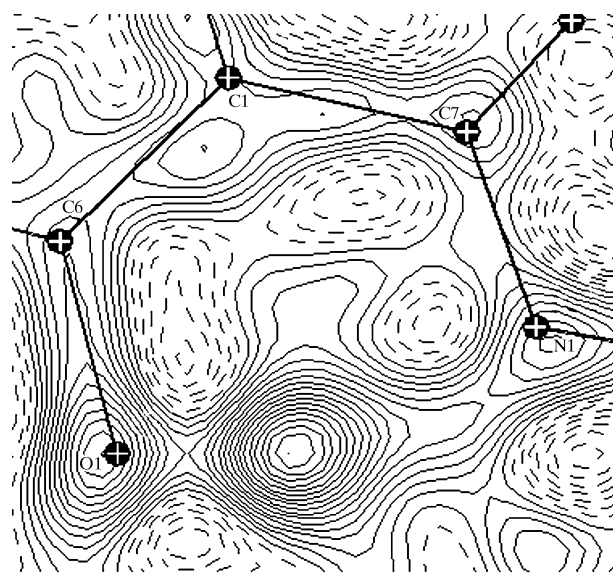

Figure 2
Difference electron-density map for (I) at 120 K. The map clearly reveals a peak assigned to one H atom connected to O1. (Contour interval 0.03 e Å^{-3}.)
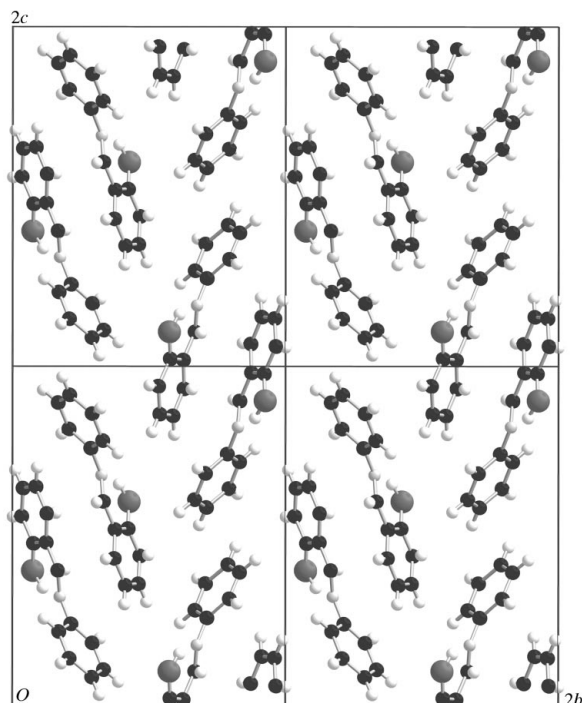
Figure 3
The packing arrangement in the plane (0*kl*) of the α_2-polymorph of salicylideneaniline.

compounds and no significant change could be detected: from 10 to 9.9° in 5-methoxysalicylaldimine (Popovic *et al.*, 2002) and from 0.7 to 1.1° in 5-chlorosalicylideneaniline (mean value; Bregman, Leiserowitz & Schmidt, 1964). Therefore, the variation may not only be due to temperature variation but, more probably, the changes are more significant for a non-planar compound.

Flat molecules have a characteristic packing arrangement, displaying stacks along the shortest axis in which the molecules are inclined. Within each stack, the molecular planes pack with short intermolecular distances of the order of 3.5 Å, normal to the molecular planes. In contrast with flat molecules, rotation of the anil ring out of the plane in the α-polymorphs prevents any close parallel stacking and the structure is relatively open, with molecules arranged head-to-tail (Fig. 3). This packing was also observed for the 2-bromo-, 2-iodo- and 2-chloro-SA derivatives (Bregman, Leiserowitz & Osaki, 1964; Burr & Hobson, 1969; Elmali & Elerman, 1997). All of these have the same space group as and similar cells to the α_2-polymorph.

Experimental

Crystals of (I) were obtained by recrystallization from methanol (m.p. ~322 K). The half-life of the spontaneous fading (dark reaction) of the red state is about 30 h at 298 K, a rate which is about 100 times slower than that of the α_1 crystalline form. Cycling between the yellow and red states was performed 50 000 times with no observed fatigue (Lo *et al.*, 1971). Procedures for the recrystallization of the α_1-polymorph from methanol and the α_2-polymorph from petroleum ether have been reported by Cohen *et al.* (1964).

Crystal data

$C_{13}H_{11}NO$	Mo $K\alpha$ radiation
$M_r = 197.23$	Cell parameters from 7113
Orthorhombic, $P2_12_12_1$	reflections
$a = 6.0750\ (11)$ Å	$\theta = 3.6–26.4°$
$b = 11.6306\ (15)$ Å	$\mu = 0.08\ mm^{-1}$
$c = 14.484\ (2)$ Å	$T = 120\ (2)$ K
$V = 1023.4\ (3)$ Å^3	Prism, yellow
$Z = 4$	$0.18 \times 0.14 \times 0.06$ mm
$D_x = 1.280$ Mg m^{-3}	

Data collection

Oxford Sapphire CCD area-detector diffractometer	$R_{int} = 0.074$
	$\theta_{max} = 26.4°$
Oscillation scans	$h = -7 \rightarrow 7$
5769 measured reflections	$k = -14 \rightarrow 14$
1237 independent reflections	$l = -17 \rightarrow 18$
1004 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	H atoms treated by a mixture of
$R[F^2 > 2\sigma(F^2)] = 0.041$	independent and constrained
$wR(F^2) = 0.101$	refinement
$S = 1.02$	$w = 1/[\sigma^2(F_o^2) + (0.0566P)^2]$
1237 reflections	where $P = (F_o^2 + 2F_c^2)/3$
140 parameters	$(\Delta/\sigma)_{max} < 0.001$
	$\Delta\rho_{max} = 0.18$ e Å^{-3}
	$\Delta\rho_{min} = -0.19$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1$A$$\cdots$N1	1.02 (3)	1.74 (4)	2.615 (3)	145 (3)

Since O, N, C and H atoms do not possess a high enough enantiomorph discriminating capacity with Mo radiation, 827 Friedel pairs were merged. The hydroxylic H atom was located in a difference electron-density (Fourier) map at the end of the refinement procedure and was refined isotropically. Carbon-bound H atoms were placed in calculated positions, with C—H distances of 0.93 Å, and then refined using a riding model, with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2003); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2003); data reduction: *XPREP* (Siemens, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *XP* (Siemens, 1998); software used to prepare material for publication: *SHELXL97*.

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