The \(a_2\)-polymorph of salicylideneaniline

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Received 7 February 2005
Accepted 22 March 2005
Online 23 April 2005

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 photochromic polymorph, which will be discussed in a subsequent paper. We report here the structure of the \(a_2\)-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 photoreactivity (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).

\[ \text{(I)} \]

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 \(a_2\)-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 \(a_1\)-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 \(a_1\)-polymorph are very different from our values for the \(a_2\)-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.

\[ \text{Figure 1} \]

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.

\[ ^{1}\text{The systematic name for salicylideneaniline is 2-(phenyliminomethyl)phenol. Alternative names that have already been reported are 2-hydroxybenzylideneaniline or phenylsalicylaldimine.} \]
A bond length of 1.281 (3) Å, with increasing O1–H1 distance of 1.02 (4) Å and the C6–O1–H1A 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 atom 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 Pbc21; 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 α2-polymorph is 54.1° at 120 K, compared with 51.4° at room temperature. In the α1 form, Destro et al. (1978) reported 49°. Only two other cases relating to this study were found. However, they concern planar...
polymorphs and no significant change could be detected: from 10 to 9.9° in 5-methoxy salicylaldehyde (Popovic et al., 2002) and from 0.7 to 1.1° in 5-chlorosalicylaldehyde (mean value; Bregman, Leiserowitz and 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-ido- and 2-chloro-SA derivatives (Bregman, Leiserowitz and Osaki, 1964; Burr and Hobson, 1969; Elmali and Elerman, 1997). All of these have the same space group as and similar cells to the α2-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 α1 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 α1-polymorph from methanol and the α2-polymorph from petroleum ether have been reported by Cohen et al. (1964).

Figure 3
The packing arrangement in the plane (0kl) of the α2-polymorph of salicylidene aniline.

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

<table>
<thead>
<tr>
<th>D—H···A</th>
<th>D—H</th>
<th>H···A</th>
<th>D···A</th>
<th>D—H···A</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1—H1A···N1</td>
<td>1.02 (3)</td>
<td>1.74 (4)</td>
<td>2.615 (3)</td>
<td>145 (3)</td>
</tr>
</tbody>
</table>

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 hydroxyl 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 Uiso(H) = 1.2Ueq(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.

The authors are grateful to the Swiss National Science Foundation for research grants (project No. 21-66916.01).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ1198). Services for accessing these data are described at the back of the journal.

References


