

Crystal Structure and Conformation of N-(5-Chlorosalicylidene)-2-hydroxy-5-chloroaniline

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N-(5-Chlorosalicylidene)-2-hydroxy-5-chloroaniline was synthesized and its crystal structure determined. It crystallizes in the orthorhombic space group $Pna2_1$ with $a = 14.668(4)$, $b = 6.084(3)$, $c = 27.980(4)$ Å, $R = 0.051$ for 4788 independent reflections). There are two independent nearly planar molecules in the asymmetric unit. The intramolecular hydrogen bonds occur between the pairs of atoms N1 and O1 [2.553(6) Å], N1 and O2 [2.585(5) Å], N2 and O3 [2.567(6) Å], N2 and O4 [2.620(5) Å], the hydrogen atoms essentially being bonded to the nitrogen atoms. The neighboring molecules are linked via an intermolecular O-H...O hydrogen bond [2.557(5) Å]. Conformations of the title compound were investigated by semi-empirical quantum mechanical AM1 calculations. The optimized geometry of the molecular structure corresponding to the nearly planar conformation is the most stable conformation in the calculations. The results strongly indicate that the minimum energy conformation is primarily determined by non-bonded steric interactions.

Introduction

Schiff bases have been used extensively as ligands in the field of coordination chemistry. Some of the reasons are that the intramolecular hydrogen bonds between the O and the N atoms which play an important role in the formation of metal complexes, and that Schiff base compounds show photochromism and thermochromism in the solid state by proton transfer from the hydroxyl O atom to the imine N atom [1, 2]. Photochromism and thermochromism are produced by the intramolecular proton transfer associated with a change in π -electron configuration [3 - 5]. Photochromic compounds are of great interest for the control and measurement of radiation intensity, optical computers and display systems [6, 7].

On the basis of structural studies on photochromic and thermochromic salicylaldimine derivatives it was concluded that the significant differences lie in the manner of molecular packing in the lattice. Molecules exhibiting thermochromy are planar while those with photochromy are non-planar [8]. Photochromic salicylideneanilines are packed rather loosely in the crystal, in which non-planar molecules may un-

dergo some conformational changes, while thermochromic salicylideneanilines are packed tightly to form one-dimensional columns. Intramolecular hydrogen bonds (either N-H...O or N...H-O) can exist in aldimine compounds derived from aromatic aldehydes having a hydroxyl group in position 2 relative to the aldehyde group [9]. The existence of the enol (or predominantly enol) tautomer has been established in all crystal structures of N-substituted salicylaldimines listed so far in the Cambridge Structure Database [9]. With the aim of gaining a deeper insight into the structural aspects responsible for the observed solid state phenomenon a conformational and crystallographic analysis of the title compound has been carried out.

Experimental Section

Preparation

The Schiff base, N-(5-chlorosalicylidene)-2-hydroxy-5-chloroaniline, was synthesized by reaction of 5-chlorosalicylaldehyde and 2-amino-4-chlorophenol at r. t.. For the preparation of the ligand, 2 mmol 5-chlorosalicylaldehyde was dissolved in 50 ml of methanol and a solution of 1 mmol of 2-amino-4-chlorophenol in 30 ml of methanol was added. The mixture was refluxed for 3 h. The solution

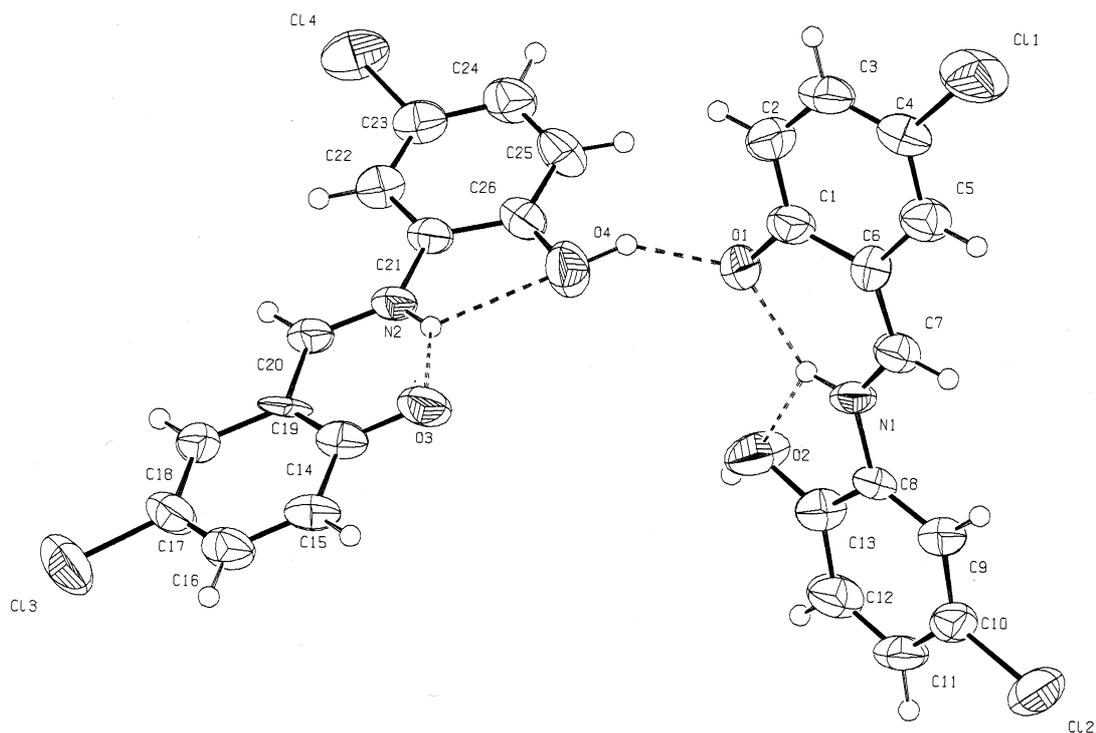


Fig. 1. The molecular structure of the title compound. Displacement ellipsoids are plotted at the 50% probability level.

was allowed to evaporate at r. t. to give red crystals, which were collected and washed with ethanol.

X-ray crystallography

X-ray data collection was performed at 303(2) K on an Enraf-Nonius CAD-4 diffractometer using a single crystal with dimensions $0.40 \times 0.15 \times 0.10$ mm with graphite-monochromated Mo- K_{α} radiation ($\lambda = 0.71093$ Å). Orientation matrix and the unit cell parameters from the setting angles of 25 centered reflections: orthorhombic, space group $Pna2_1$, $a = 14.668(4)$, $b = 6.084(3)$, $c = 27.980(4)$ Å, $V = 2496.9(2)$ Å³, $Z = 8$, $d_{\text{calcd}} = 1.501$ Mg/m³, $F(000) = 1152$, $\mu = 0.452$ mm⁻¹. Three standard reflections (-200 , -210 , -130) were measured every 7200 s and the orientation of the crystal was checked after every 300 reflections. These intensity measurements did not indicate any variations in the experimental conditions, but a decrease in the intensity of the standard reflections indicated a decay of 2.4% of the crystal. The structure was solved by direct methods using the SHELX-97 [10] program and refined by full-matrix least-squares procedures on F^2 using SHELX-97 [11] with allowance for anisotropic thermal motion of all non-hydrogen atoms. All hydrogen positions (except hydrogen atoms from O and N) were calculated using a riding model. The hy-

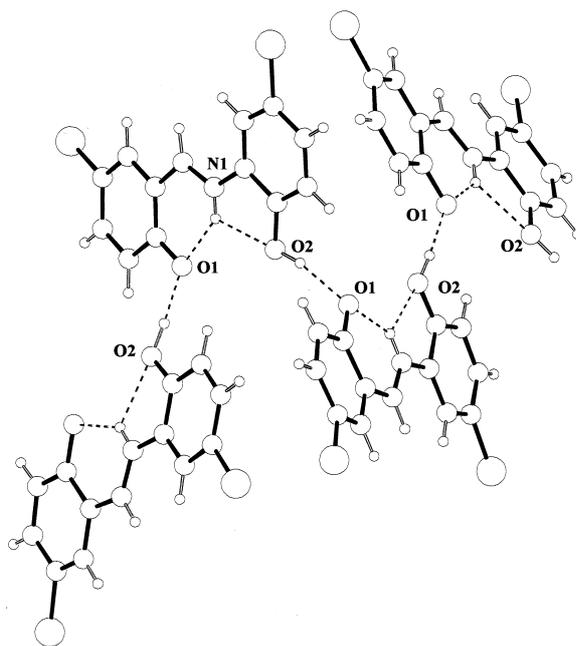


Fig. 2. Crystal packing diagram for the title compound.

drogen atoms from O and N atom were found from the difference Fourier maps calculated at the end of the refine-

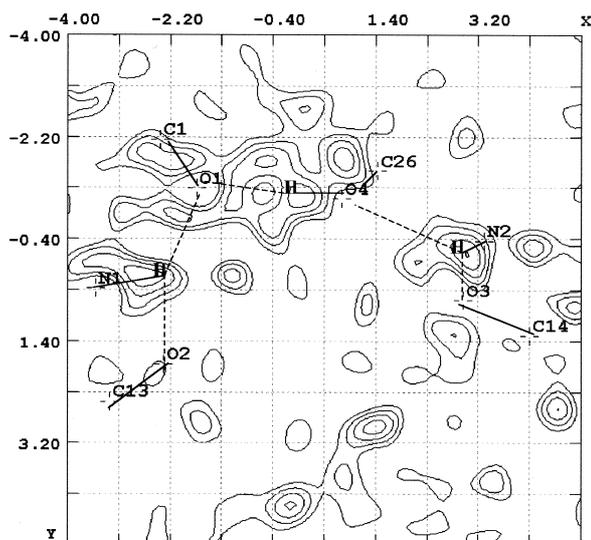


Fig. 3. Difference Fourier map.

ment process as a small positive electron density (Fig. 2 and Fig. 3). The refinement converged to $R = 0.051$, $R_w^2 = 0.125$ for all data and 332 parameters. Largest difference peak and hole are 0.276 and -0.353 eÅ^{-3} . Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, e-mail: deposit@ccdc.cam.ac.uk as supplementary publication no. CCDC 154351 [12].

Conformational analysis

Theoretical calculations were carried out with the standard parameters using MOPAC package [13] which includes the AM1 Hamiltonian [14]. Geometry optimizations of the crystal structure of the title compound were carried out using the Fletcher-Powell-Davidson algorithm [15, 16] implemented in the package and the PRECISE option to improve the convergence criteria. To determine the conformational energy profiles full geometrical optimizations were performed and values of the AM1 total energy were calculated as a function of torsion angles θ_1 (C6-C7-N1-C8) and θ_2 (C19-C20-N2-C21), varied every 5° from -180° to 180° .

Results and Discussion

Fractional atomic coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms are given in Table 1. The bond distances and the bond angles are listed in Table 2. An ORTEP and intermolecular view of the molecular struc-

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$). $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
C11	2657(2)	1199(1)	980(1)	88(1)
C12	-718(2)	-2017(3)	1244(1)	72(1)
C13	-118(2)	-7020(4)	412(1)	89(1)
C14	3245(2)	7007(4)	134(1)	76(1)
O1	1429(3)	7369(6)	2689(1)	56(2)
O2	-92(3)	3300(9)	2949(1)	80(2)
O3	1028(3)	-2290(6)	-1305(1)	59(2)
O4	2570(2)	1777(8)	-1574(1)	67(1)
N1	638(2)	4559(6)	2154(1)	41(1)
N2	1853(3)	478(6)	-764(1)	42(1)
C1	1744(3)	8387(9)	2303(1)	50(1)
C2	2239(4)	1031(1)	2331(2)	56(2)
C3	2512(4)	1139(1)	1926(2)	56(2)
C4	2311(4)	1056(1)	1482(2)	55(2)
C5	1857(4)	8642(11)	1436(2)	53(2)
C6	1542(4)	7470(8)	1840(3)	37(2)
C7	1019(3)	5600(7)	1788(1)	46(1)
C8	98(6)	2652(9)	2135(3)	42(2)
C9	-59(3)	1467(10)	1726(2)	45(1)
C10	-563(4)	-467(9)	1758(2)	50(1)
C11	-926(4)	-1166(11)	2181(2)	54(1)
C12	-786(4)	111(11)	2586(2)	61(2)
C13	-273(5)	2043(11)	2570(2)	50(2)
C14	757(3)	-3311(9)	-910(1)	46(1)
C15	257(4)	-5308(10)	-949(2)	53(1)
C16	-9(4)	-6386(11)	-542(2)	55(2)
C17	202(4)	-5518(10)	-91(2)	54(2)
C18	662(3)	-3592(11)	-50(2)	47(1)
C19	949(6)	-2502(7)	-466(3)	49(3)
C20	1469(3)	-553(7)	-397(1)	44(1)
C21	2402(6)	2373(9)	-752(3)	41(2)
C22	2562(3)	3569(10)	-350(2)	46(1)
C23	3072(4)	5383(10)	-378(2)	51(2)
C24	3430(4)	6145(12)	-800(2)	57(2)
C25	3294(4)	4884(11)	-1207(2)	62(2)
C26	2774(5)	3035(9)	-1191(2)	52(2)

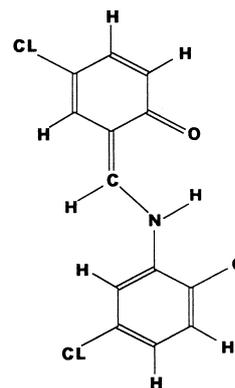
ture of the title compound is given in Fig. 1 and Fig. 2 [17].

Thermochromic and photochromic properties of the salicylideneanilines are a function of the crystal and molecular structure [3]. On the basis of structural studies on salicylaldimine derivatives it was concluded that the significant differences are related to the manner of molecular packing in the crystal. Molecules exhibiting thermochromy are planar while those showing photochromy are non-planar [18]. There are two independent molecules in the asymmetric unit and both of them are nearly planar. The angles between the

Table 2. Bond lengths (Å) and angles (°) with e. s. d. in parentheses.

O1-C1	1.328(1)	C1-C2	1.378(8)
C1-C6	1.441(9)	C2-C3	1.371(8)
C4-Cl1	1.728(6)	C3-C4	1.373(8)
C7-N1	1.328(1)	C4-C5	1.349(8)
N1-C8	1.406(7)	C5-C6	1.416(9)
C8-C9	1.370(10)	C6-C7	1.380(7)
C9-C10	1.392(8)	C8-C13	1.386(10)
C10-C11	1.367(8)	C10-Cl2	1.735(6)
C11-C12	1.388(9)	C14-C19	1.366(10)
C12-C13	1.396(9)	C15-C16	1.370(9)
C13-O2	1.334(6)	C16-C17	1.404(9)
O3-C14	1.328(1)	C17-C18	1.357(8)
C14-C15	1.423(8)	C18-C19	1.404(10)
C17-Cl3	1.741(6)	C19-C20	1.423(7)
C20-N2	1.328(1)	C21-C26	1.404(10)
N2-C21	1.407(8)	C23-Cl4	1.758(6)
C21-C22	1.359(10)	C26-O4	1.350(1)
C22-C23	1.336(8)	C25-C26	1.360(8)
C23-C24	1.373(8)	C24-C25	1.387(9)
O1-C1-C2	122.2(5)	C3-C4-Cl1	119.1(5)
O1-C1-C6	118.6(5)	C5-C4-C3	120.7(5)
C2-C1-C6	119.2(4)	C7-C6-C5	120.7(6)
C2-C3-C4	120.7(6)	C5-C6-C1	117.1(5)
C3-C2-C1	120.9(5)	C7-N1-C8	127.0(5)
C5-C4-Cl1	120.2(5)	C9-C8-N1	124.1(7)
C4-C5-C6	121.4(5)	C8-C9-C10	118.8(6)
C7-C6-C1	122.0(5)	C11-C10-Cl2	119.9(5)
N1-C7-C6	123.0(5)	C10-C11-C12	118.4(5)
C9-C8-C13	121.8(6)	O2-C13-C8	117.9(6)
C13-C8-N1	114.1(6)	C8-C13-C12	117.7(6)
C11-C10-C9	121.6(5)	O3-C14-C19	121.7(5)
C9-C10-Cl2	118.5(5)	C19-C14-C15	119.0(4)
C11-C12-C13	121.7(6)	C15-C16-C17	120.3(6)
O2-C13-C12	124.5(6)	C18-C17-Cl3	121.3(5)
O3-C14-C15	119.3(5)	C17-C18-C19	119.2(6)
C16-C15-C14	119.4(5)	C14-C19-C20	122.3(6)
C18-C17-C16	120.7(5)	N2-C20-C19	121.1(5)
C16-C17-Cl3	118.0(5)	C22-C21-C26	120.2(6)
C14-C19-C18	121.4(5)	C26-C21-N2	115.9(6)
C18-C19-C20	116.2(7)	C22-C23-C24	122.9(5)
C20-N2-C21	127.7(5)	C24-C23-Cl4	117.1(5)
C22-C21-N2	123.9(7)	C26-C25-C24	120.7(5)
C23-C22-C21	119.5(6)	O4-C26-C21	116.4(5)
C22-C23-Cl4	119.9(5)		
C23-C24-C25	117.7(6)		
O4-C26-C25	124.6(5)		
C25-C26-C21	118.9(5)		

planar moieties (C1-C2-C3-C4-C5-C6-C7-O1-Cl1 and C8-C9-C10-C11-C12-C13-O2-N1-Cl2, C14-C15-C16-C17-C18-C19-C20-O3-Cl3 and C21-C22-C23-C24-C25-C26-O4-N2-Cl4) are 10.9(2) and 11.9(2)°, respectively. Two types of intramolecular hydrogen bonding (either N...H-O or N-H...O)



Scheme 1.

can exist in Schiff bases. The crystal structure is stabilized by intermolecular hydrogen bonds. The crystal structure determination indicates the existence of both N1-H1...O1 and N1-H1...O2 and both N2-H2...O3 and N2-H2...O4 bifurcated intramolecular hydrogen bonds as follows: N1...O1 2.553(6) Å, N1...O2 2.585(5) Å, N2...O3 2.567(6) Å and N2...O4 2.620(5) Å. These intramolecular distances are significantly shorter than the sum of the van der Waals radii of nitrogen and oxygen atoms [20]. The hydrogen atoms were located at the end of the refinement process from a difference Fourier map as well defined small electron density maxima (Fig. 3). O1-C1 [1.328(1) Å] and O3-C14 [1.328(1) Å] bond distances were determined to be of bond order 1.5 from the values of the single and double C-O bonds [21]. This along with the very short C2=C3 [1.371(8) Å] and C15-C16 [1.370(9) Å] suggests the presence of a significant keto tautomer. Clearly, the keto tautomer is favoured over the enol form (Scheme 1).

In order to define the conformational flexibility of the title molecule, semi-empirical calculations using the AM1 molecular orbital method were carried out. The AM1 optimized geometry and conformations are in agreement with those crystallographically observed. The energy profiles of the θ_1 (C6-C7-N1-C8) and θ_2 (C19-C20-N2-C21) torsion angles show one maximum at nearly 330° and 25°, respectively (see Fig. 4). The energy barriers arise from the steric interactions between O1 and C9 and between O3 and C22 atoms. The most stable non-planar conformation corresponds to the $\theta_1 = 25.7^\circ$ and $\theta_2 = 25.1^\circ$, respectively. Bürgi and Dunitz (1971) carried out an extensive theoretical and experimental study on the non-planar conformation of the N-benzylidene-

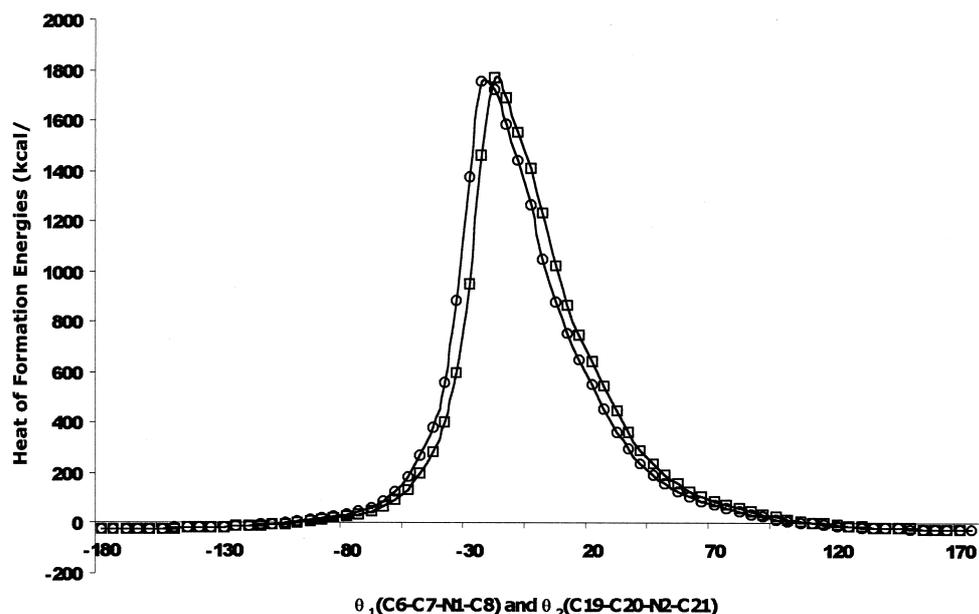


Fig. 4. AM1 calculated conformation energies for X-ray structure of the θ_1 (C6-C7-N1-C8) and θ_2 (C19-C20-N2-C21) torsion angles.

aniline and related compounds [19]. Their explanation for the non-planarity of N-benzylideneaniline involves a competition between two principal factors: (a) The interaction of the *ortho* hydrogen atom on the aniline ring and the hydrogen atom on the "bridge" carbon atom, which is repulsive in the planar conformation but is reduced with increasing non-planarity. (b) The π -electron system, itself divisible into two components, including, on the one hand, delocalization between the -CH=N- double bond and the aniline phenyl ring (which is maximized for a planar conformation) and, on the other hand, delocalization of the nitrogen lone pair electrons into the aniline ring which is essentially zero

for the planar conformation but increases with increasing non-planarity (where the lone pair density on the nitrogen may interact with the π system of the ring).

In summary, the AM1 optimized geometry of the structure of the title molecule corresponds to the nearly planar conformation as the most stable conformation in all calculations. The results indicate that the most stable conformation is primarily determined by non-bonded hydrogen-hydrogen repulsions. The interaction between the N-lone pair and the π electrons of the phenyl ring, however, might also contribute to the conformational energy.

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