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Crystal Structure of Schiff base Compound 2-[(2-chloro-4-nitrophenyl) iminomethyl] phenol

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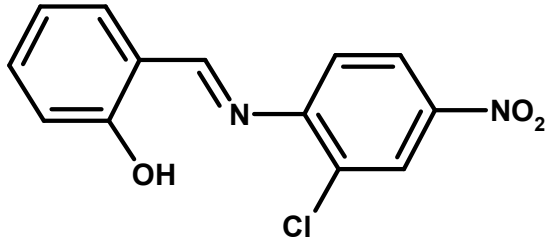
Abstract: Single crystals of Schiff base compound 2-[(2-chloro-4-nitrophenyl) iminomethyl] phenol (1) were grown by the slow evaporation technique at room temperature. The crystal structure of the title compound was determined by single crystal X-ray diffraction. The title compound crystallizes in the monoclinic system, space group $P2_1$, with two symmetry independent molecules. Intramolecular O-H···N hydrogen bonds form S(6) motifs in each molecule. Intermolecular C-H···O interactions connect the molecules into a three dimensional network.

Keywords: *Schiff base; crystal structure; monoclinic; inter- and intra-molecular interactions*.

Introduction

Recently, an interest in Schiff-bases derived from aromatic o-hydroxylaldehyde has increased significantly due to their structures [1-3] and applications [4-9]. These compounds show tautomerism via the intramolecular proton transfer from the oxygen atom of OH to the neighboring nitrogen atom of the C = N group [4]. Although, interaction between anion and o-hydroxy Schiff bases is weaker than the interaction of metal ions and o-hydroxy, several o-hydroxy Schiff bases groups used as anion receptors [6, 9]. As a continuation of our previous work on Schiff bases [10-13], in this work, we report the crystal structure of Schiff base compound N-(2-chloro-4-nitro-phenyl) salicylaldehyde-imine (1) (Scheme1).



Scheme 1 Chemical structure of 2-[(2-chloro-4-nitrophenyl) iminomethyl] phenol (**1**).

Experimental

All reagents and solvents for synthesis and analysis were commercially available and used as received.

Synthesis of 2-[(2-chloro-4-nitrophenyl) iminomethyl] phenol (1)

The preparation of 1 was done according to published method [14, 15]. A solution of salicylaldehyde (0.01 mol) in 25 ml methanol was stirred for about 10 min. To this stirring solution, a solution of 2-chloro-4-nitroaniline (0.01 mol) in 20 ml methanol was added dropwise under constant stirring. The mixture was refluxed for 2 h and then allowed to cool overnight to the room temperature. Yellow crystals were grown by the slow evaporation technique at the room temperature. Yield: 84%. FT-IR (cm^{-1}, KBr). 3352 υ (OH or H_2O), 1621 υ (C = N), 1278 υ (C-O), 1394 υ (C-O), 1565 Ph ring C = C.

X-ray crystallography

Crystallographic measurements were done at 120 K with four circle CCD diffractometer Gemini of Oxford diffraction, Ltd., with mirrors-collimated Cu Kα radiation (λ = 1.54184 Å). The crystal structure was solved by direct methods with program SIR2002 [16] and refined with the Jana2006 program package [17] by full-matrix

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least-squares technique on F^2. Hydrogen atoms were mostly discernible in difference Fourier maps and could be refined to reasonable geometry. According to common practice bonded to carbon kept in ideal positions during the refinement while positions of hydrogen atoms of hydroxyl groups were freely refined with a distance restraint 0.85 Å. The isotropic atomic displacement parameters of hydrogen atoms were evaluated as $1.2U_{eq}$ of the parent atom. Crystallographic data and details of the data collection and structure refinements are listed in Table 1.

The sample used for the measurement was twinned with twinning operation 180 ° rotation about c*. This leads to the twinning matrix -1 0 0 (the first row) / 0 -1 0 / 0.5 0 1 applied to the column of the indices and, in the diffraction pattern, it generates only fully overlapped and fully separated reflections. Therefore, we could use for the refinement the stronger domain and the twinning matrix to scale the fully overlapped reflections.

The structure was found to be non-centrosymmetric. The missing center of symmetry was used as an additional twinning operation, thus generating a four-fold twin from the original two-fold twin: twin domain A [twinning operation 1 0 0 / 0 1 0 / 0 0 1, refined volume fraction 0.428(18)]; twin domain B [twinning operation -1 0 0 / 0 -1 0 / 0 0 -1 refined volume fraction 0.146(11)]; twin domain A′, [twinning operation -1 0 0 / 0 -1 0 / 0 0 -1 refined volume fraction 0.304(9)] and twin domain B′, [twinning operation 1 0 0 / 0 1 0 / 0 0 1 refined volume fraction 0.122(11)]. The ratio of the twinning fractions between the original and inverted twin domain is 0.710 for A′:A and 0.836 for B:B′. These numbers can be understood as partial Flack parameters. The molecular structure plots were prepared by ORTEP III [18].

Table 1 Crystallographic and structure refinement of **1**.

Empirical formula	$C_{13}H_9ClN_2O_3$
Formula weight	276.67
Crystal size (mm^3)	0.40 × 0.09 × 0.08
Crystal system	Monoclinic
Space group	$P2_1$
Density (gcm^{-3})	1.5368
wave lenght	1.5418 (Cu $K\alpha$)
T (K)	1.5418
a (Å)	120
b (Å)	7.3144(2)
c (Å)	11.8839(3)
β (°)	13.8725(4)
V ($Å^3$)	97.546(2)
Z	1195.40(6)
μ (mm^{-1})	4
T_{min}	2.90
T_{max}	0.492
Measured reflections	1.0
Independent reflections	14843
Reflection with $I \geq 3\sigma(I)$	4222
R_{int}	4165
S	0.024
Goodness of fit	1.61
F(000)	1.62
$R[F^2>3\sigma(F^2)]$	568
$wR(F^2)$	0.031
Flack parameter	0.080
Parameters	0.71, 0.84
$\Delta\rho_{max}$ ($eÅ^{-3}$)	352
$\Delta\rho_{min}$ ($eÅ^{-3}$)	0.13
Theta range for data collection	-0.12
	3.21-67.02

Results and Discussion

The title compound 1 was obtained in high yield, 84%, by mixing equimolar amounts of salicylaldehyde and 2-chloro-4-nitroaniline. It was stable in the solid state for several days. The title compound is very slightly soluble in common organic solvents such as acetonitrile and methanol but completely soluble in chloroform and dichloromethane.

An ORTEP view of the structure of 1 obtained by the single-crystal X-ray diffraction is shown in Fig. 1. Compound 1 crystallizes in the space group $P2_1$ with two molecules in the asymmetric unit (Fig. 1).

Selected bond distances and angles of 1 are listed in Table 2. Bond distances and angles around C=N group are in good agreement with those reports in similar o-hydroxy Schiff base compounds [1-5,7,9,10]. The molecule of 1 is non-planar, with a dihedral angle between the two aromatic rings of 40.906(63)° and 39.642(67)° for the two symmetry independent cases. The bond distances of N1=C7 (1.291(3) Å), N3=C20 (1.291(3) Å), N1-C1 (1.401(3) Å) and N3-C14 (1.396(3) Å) are consistent with double and single bonds, respectively [1-5,7,9,10]. The bond angles C8-C7-N1 (121.3(2)°), C7-N1-C1 (119.92(19)°), C21-C20-N3 (121.3(2)°) and C20-N3-C14 (120.7(2)°) consistent with the sp^2 hybrid character for C7, N1, C20 and N3 [1-5,7,9,10].

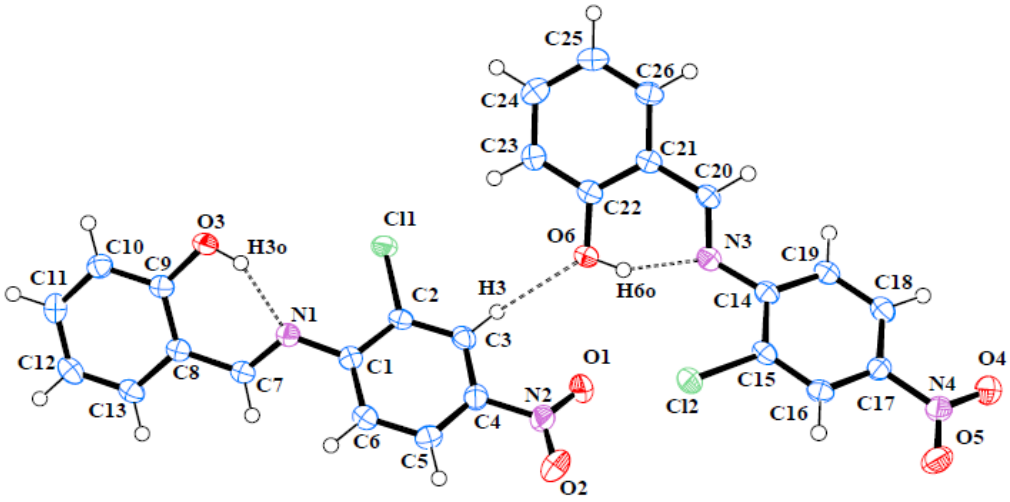

Fig. 1 The molecular structure of N-(2-chloro-4-nitro-phenyl)salicylaldehyde-imine with displacement ellipsoids drawn at 50% probability level. The H-bonds are indicated as dashed lines.

Table 2 Selected bond distances (Å) and angles (°) of 1.

Cl1-N1	2.941(2)	N1-C1	1.401(3)
Cl2-N3	2.935(2)	N1-C7	1.291(3)
O1-N2	1.227(3)	N2-C4	1.464(3)
O2-N2	1.226(3)	N3-C14	1.396(3)
O4-N4	1.225(3)	N3-C20	1.291(3)
O5-N4	1.227(3)	N4-C17	1.461(3)
Cl1 N1 C1	66.91(11)	Cl1 N1 C7	146.15(14)
C1 N1 C7	119.92(19)	O1 N2 O2	124.2(2)
O1 N2 C4	118.1(2)	O2 N2 C4	117.7(2)
Cl2 N3 C14	66.67(12)	Cl2 N3 C20	144.78(14)
C14 N3 C20	120.7(2)	O4 N4 O5	123.7(2)
O4 N4 C17	118.2(2)	O5 N4 C17	118.12(19)
N1 C1 C2	118.5(2)	N1 C1 C6	123.2(2)
N2 C4 C3	118.1(2)	N2 C4 C5	118.7(2)
N1 C7 C8	121.3(2)	N3 C14 C15	118.9(2)
N3 C14 C19	122.7(2)	N4 C17 C16	119.0(2)
N4 C17 C18	118.7(2)	N3 C20 C21	121.3(2)

The most pronounced feature causing the deviation from the non-centrosymmetric structure is the rotation of the NO_2 group with respect to the adjacent aromatic ring, 5.437(106)° and 14.055(82)° for the two symmetry independent cases. We did also a simple test how similar are the two molecules with respect to the measured data. One of the molecules was described as a rigid body and we refined its atomic parameters plus translation and rotation transforming this molecule to the second molecule. Thus, in the test we refined two identical molecules. The R value increased from 0.031 to 0.057 and goodness of fit increased from 1.61 to 3.83 (using the same weighting scheme for both attempts). This means that the molecules are very similar but the data still allows for their distinction.

Ortho position of the hydroxyl group to the imine group of Schiff base due to the existence of O-H···N hydrogen bond and tautomerism between enol-imine and keto-amine form [1,2,4,10]. Another inter-molecular non-classical hydrogen bonds of C-H···O (Table 3, Figs. 1,2) connect the adjacent molecules to one-dimensional supramolecular structure. Therefore, the hydrogen bonds of 1 probably play an important role in the molecular and crystal stabilities [5,11].

Table 3 Hydrogen-bond geometry (Å, °).

D-H···A	D-H	H···A	D···A	D-H···A
N1···H3-O3	0.845	1.836	2.591	147.955
N3···H6-O6	0.850	1.824	2.608	152.682
C3···H3-O6	0.960	2.663	3.307	124.832
C24-H24···O4	0.960	2.551	3.252	130.025
C1-H11···O2	0.960	2.565	3.267	130.164

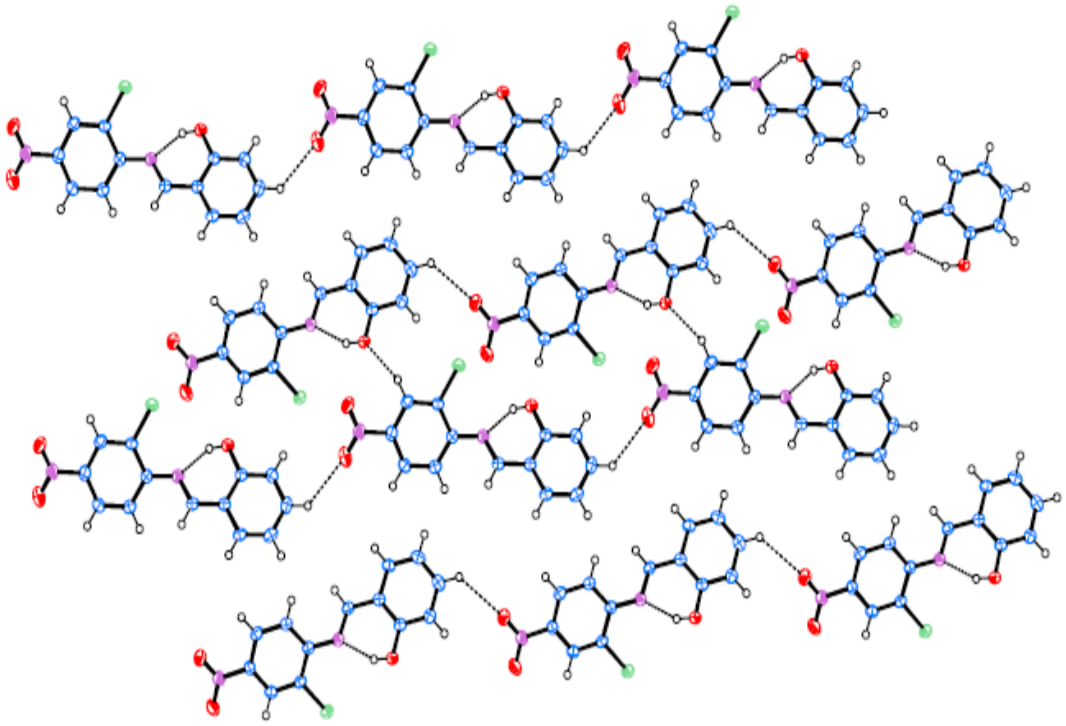

Fig. 2 The crystal packing of 1, as seen along the c axis. Hydrogen bonds are shown as dashed lines.

Supplementary data

Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Center, CCDC Nos. 940662. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk or http:www.ccdc.cam.ac.uk.

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