

Redetermination of Crystal Structure of N,N'-bis (2-Hydroxybenzylidene)-2,2-Dimethyl-1,3- Propanediamine

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ABSTRACT: The structure of N,N'-bis(2-hydroxybenzylidene)-2,2-dimethyl-1,3-propanediamine, $C_{19}H_{22}N_2O_2$, has been studied at low temperature (120K) by means of single-crystal X-ray diffraction. Solving the structure shows an orthorhombic unit cell, with $P2_12_12_1$ space group, $Z = 4$, $a = 6.1046$ (4) Å, $b = 15.8349$ (11) Å, $c = 17.2898$ (12) Å and $V = 1671.3$ (2) Å³. There are two relatively strong hydrogen bonds (average O—H...N, 2.59 Å), involving the hydroxyl group and the nearest N atom of the imine groups is an indicative of intra-molecular hydrogen bonding within each salicylideneimine moiety. C-H... π interactions connect the neighboring molecules together, stabilizing the crystal network. No significant π - π interactions are present in the crystal structure.

KEYWORDS: Schiff base, Crystal structure, Single crystal X-ray diffraction, Hydrogen bonding, C-H... π interaction.

INTRODUCTION

Schiff base compounds were discovered by *Hugo Schiff* in 1864 [1]. During the past two decades, considerable attention has been paid to the chemistry of Schiff base containing nitrogen ligands and their transition metal complexes [2-4]. Schiff bases derived from salicylaldehydes (salens) are known to form stable complexes with most transition metal ions, which are of interest in bioinorganic chemistry. Schiff bases show biological activities including antibacterial, antifungal, anticancer, and herbicidal

properties and are a class of important compounds in medicinal and pharmaceutical fields [5,6]. They are also utilized as starting materials in the synthesis of industrial compounds [7] and are reagents, which can play an important role in the dye and plastic industries as well as for liquid crystal technology and physiology [8,9]. These compounds can be easily obtained from a simple condensation reaction of carbonyl and amino groups in different compounds [10,11].

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Table 1: Crystallographic data for (I) at 120 K and the previously similar reported structure at room temperature (II) [12].

	I	II
Formula	C ₁₉ H ₂₂ N ₂ O ₂	
M	310.39	
Crystal system	Orthorhombic	
Space group	P2 ₁ 2 ₁ 2 ₁	
a / Å	6.1046 (4)	6.160(4)
b / Å	15.8349 (11)	16.172(6)
c / Å	17.2898 (12)	17.307(7)
V / Å ³	1671.3 (2)	1724.1(15)
T / K	120 (2)	293(2)
Z	4	
D _{calcd} / g.cm ⁻³	1.234	1.196
μ(Mo-K α) / mm ⁻¹	0.081	0.078
Crystal size / mm	0.10×0.15×0.45	0.21×0.28×0.32
Measured reflections	19332	7793
Unique reflections	2770	2677
Observed reflections	2466	1163
Θ / °	1.74-25.99	2.35-25.00
h _{min, max}	-8, 8	-4, 6
k _{min, max}	-22, 22	-18, 17
l _{min, max}	-23, 23	-19, 18
R _{int}	0.0336	0.0859
Final R ₁ ,wR ₂	0.0371,0.0936	0.0378,0.0640
(all data)	0.0396,0.0955	0.1045, 0.0773

The title compound was previously reported at ambient temperature [12]. Due to the estimated Flack parameter in the final structure factor summation [13], absolute configuration did not determine precisely. In the current study, we prompted to obtain a better crystal quality and re-measure the title compound at low temperature to refine the absolute structure.

EXPERIMENTAL SECTION

Chemicals

The title compound (I) was prepared *via* condensation reaction of 1,3-diamino-2,2-dimethyl propane and salicylaldehyde, according to the literature [12].

X-ray Diffraction Analysis

The data collections at low temperature were made by means of a SMART Bruker diffractometer equipped with

a CCD area detector. No intensity variations due to decomposition of the crystals were observed. Selected crystallographic and experimental details are summarized in Table 1.

Data reduction and multi-scan absorption correction were performed, using the Bruker program packages SAINT and SADABS, respectively [14]. The structure was solved by direct methods using SHELXS-97, and refined using full-matrix least-squares method on F², SHELXL-97 [15]. Molecular graphics were drawn by Diamond and Mercury programs [16] and PLATON software [17] was used to prepare materials for publication.

All non-hydrogen atoms were refined anisotropically. Aromatic and methyl H atoms were placed in calculated positions (C-H = 0.93 Å, C-H = 0.96 Å, respectively) and constrained to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = 1.2$ and $1.5 U_{\text{eq}}(\text{C})$, respectively. Methylene, methine, and

Table 2: Hydrogen-bond geometries (Å).

D—H...A	D—H	H...A	D...A	D—H...A
O1—H1...N1	0.92 (3)	1.77 (3)	2.598 (2)	148 (3)
O2—H2...N2	0.97 (3)	1.67 (3)	2.580 (2)	154 (3)

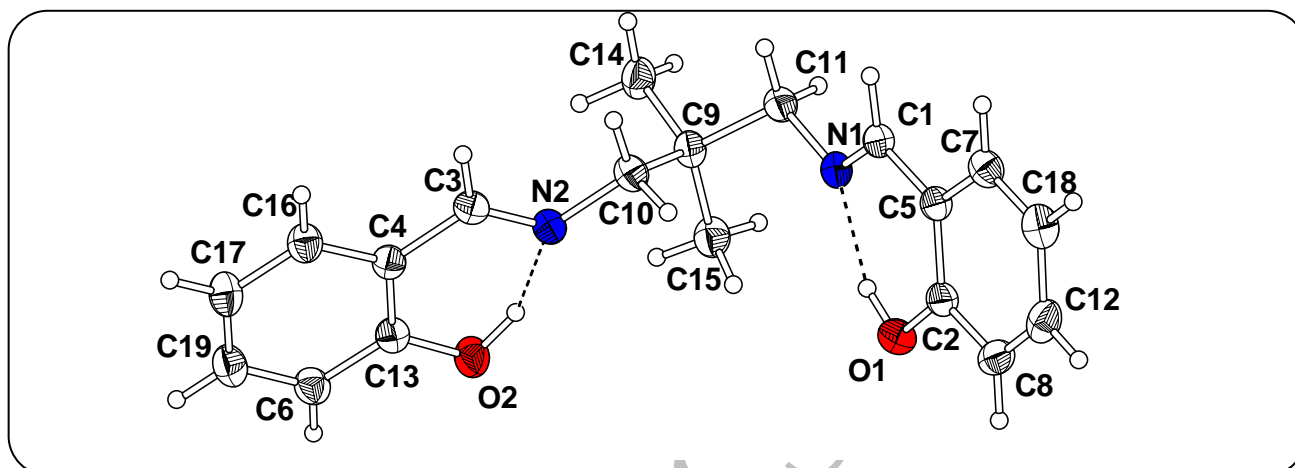


Fig. 2: ORTEP diagram of the Schiff base ligand, showing 50% probability ellipsoids. Hydrogen atoms are shown with arbitrary circles.

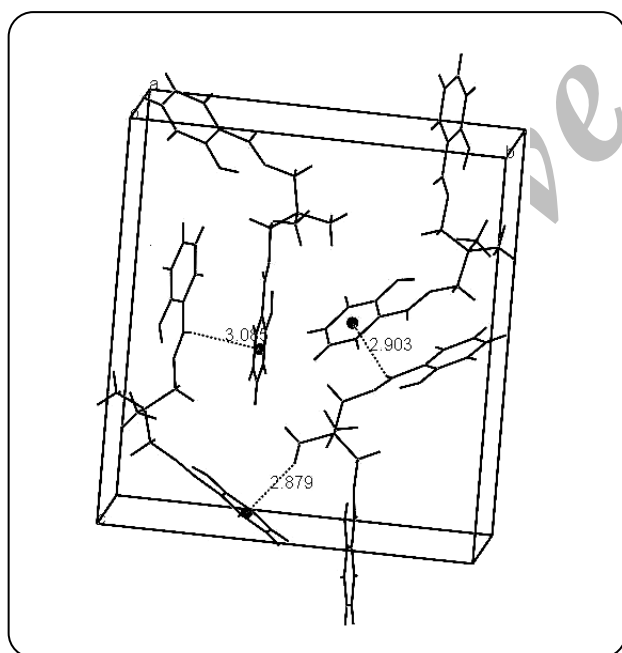


Fig. 3: Packing view of the ligand in the unit cell, C-H π interactions are shown by dashed line.

hydroxyl H atoms were located in difference electron density maps and their coordinates were refined freely with $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{C \& O})$.

RESULTS AND DISCUSSION

The molecular structure of (I) and the atom-numbering scheme are shown in Fig. 2. It is described in orthorhombic system with space group $P2_12_12_1$ and four molecules in each unit cell. It contains two N-methylsalicylalimine and two methyl groups, connected to a carbon atom in a distorted tetrahedral configuration. The two phenyl rings are of course planar with dihedral angle of $69.2 (1)^\circ$, resulting in an inappropriate conformation for quadridentate ligand activity. Relatively strong intra-molecular hydrogen bonds are present between the hydroxyl group (O1 & O2) and the nearest N atom (N1 & N2) in the imine groups (Fig. 2 & Table 2). The C-H... π interactions with an average distance of 2.86 \AA hold the neighboring molecules together, stabilizing the crystal structure (Fig. 3). No significant π - π interactions are found in the crystal structure.

The O1-C2 and O2-C13 bond lengths of $1.352(2)$ and $1.353(2) \text{ \AA}$, respectively, are consistent with O-C single bond. Likewise, the N1-C1 and N2-C3 bond distances with $1.282(2)$ and $1.278(2) \text{ \AA}$, respectively, are in accordance with $\text{N}=\text{C}$ double bond (Table 3). Selected bond length and angles are summarized in Table 3, and Table 4 shows the final coordinates and displacement parameters of non-hydrogen atoms.

Table 3: Selected bond length (Å) and angles (°).

N1-C1	1.282 (2)	C1-N1-C11	119.06 (17)
N1-C11	1.462 (2)	C3-N2-C10	119.76 (17)
N2-C3	1.278 (2)	C13-O2-H2	103.3 (17)
N2-C10	1.457 (2)	N1-C1-C5	120.91 (18)
O1-C2	1.352 (2)	N1-C11-C9	111.86 (15)
O2-C13	1.353 (2)	O2-C13-C6	118.78 (17)
O1-H1	0.92 (3)	O2-C13-C4	121.55 (16)

Comparing the O1...O2 and N1...N2 distances of 6.56 and 4.25 Å, respectively in the current structure with the corresponding value of 2.73 and 2.92 Å when coordinated to Mo^{VI} [18], clearly shows inappropriate conformation of the title structure for direct coordination to a metal ion.

As expected, the obtained data at low temperature have lower atomic movements, indicating lower thermal parameters in comparison to the data at room temperature. Moreover, the obtained Flack parameter value close to zero by the program in the final structure factor calculation of this study is a strong indication that the absolute structure is correct.

Supplementary Material

CCDC- 702754 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallography Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033; e-mail: deposit@ccdc.cam.ac.uk

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