# ORIGINAL PAPER

# One Dimensional Hydrogen Bonded Arrangement in New Schiff-Base Compound (E)-2-(2,5-dimethoxybenzylideneamino) phenol (1): Synthesis, Characterization, Crystal Structure and Conformational Studies

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**Abstract** New Schiff-base compound (*E*)-2-(2,5dimethoxybenzylideneamino)phenol (**1**) was synthesized and characterized by elemental analyses, FT-IR and <sup>1</sup>H-NMR spectroscopy and single crystal X-ray diffraction. Molecular orbital calculation has been carried out for **1** by using HF method at 6-31G basis set. The title compound **1** crystallizes in monoclinic system, space group C2/c, with a = 19.4581(13) Å, b = 9.5805(5) Å, c = 13.8431(7) Å,  $\beta = 93.471(2)^\circ$ , V = 2575.9(3) Å<sup>3</sup> and Z = 8. In the crystal structure two molecules are stabilized by a pair of intermolecular O1–H1…N1<sup>i</sup> hydrogen bonds. The dimeric units are further linked via C6–H6…O3<sup>ii</sup> hydrogen bond.

**Keywords** Schiff-base  $\cdot$  Spectroscopy  $\cdot$  HF(6-31G)  $\cdot$  One-dimensional  $\cdot$  Hydrogen bonds

# Introduction

The preparation of the Schiff bases and their use as the complexation agent in the preparing of transition metal complexes have been an active area of research in recent years [1], because of their potential application in the

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K. Gotoh · H. Ishida Department of Chemistry, Faculty of Science, Okayama University, Okayama 700-8530, Japan asymmetric catalysis [2], magnetic properties [3], photochromism [4], binding with DNA [5], construction of supramolecular structures [6], activity against Ehrlich ascites carcinoma (EAC) [7], dye and pigment [8], corrosion inhibitors [9], anti-HIV [10] and physical properties in the crystalline state [11]. These properties are greatly influenced by the geometry of the Schiff-base molecules in the crystal structure [11]. Therefore the study of inter- or intra-molecular interactions in the crystal packing of various compounds is necessary and can led to design and synthesis of new materials [12–15]. Because the inter- or intra-molecular hydrogen bonds, such as N–H…N, N–H…O and O–H…O, are strong and directional they are widely used as the principle interactions in this strategy [12–17].

As an additional contribution to the synthesis, characterization and crystal structures of Schiff-base compounds and in the course of our ongoing studies of these kinds of materials [18, 19], we describe here the synthesis, characterization, crystal structures and conformational studies of new Schiffbase compound (E)-2-(2,5-dimethoxybenzylideneamino)phenol (1) (Scheme 1).

### **Experimental Procedures**

All reagents and solvents for synthesis and spectroscopic studies were commercially available and used as received without further purification. Elemental analyses were carried out using a Heraeus CHN-O-Rapid analyzer. <sup>1</sup>H-NMR spectra were measured with a BRUKER DRX-500 AVANCE spectrometer at 500 MHz and all chemical shifts are reported in  $\delta$  units downfield from TMS. The infrared spectrum was recorded on a Perkin Elmer FT-IR spectrophotometer as a KBr pellet.

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Synthesis of (E)-2-(2,5-Dimethoxybenzylideneamino)Phenol (1)

A solution of 2.5-dimethoxybenzaldehyde (3.30 g, 0.2 mmol) in 15 mL methanol was heated for 10 min at 50 °C and then stirred for about 15 min. To this stirring solution, a solution of 2-aminophenol (2.18 g, 0.2 mmol) in 10 mL methanol was added dropwise with constant stirring. The mixture was heated for 20 min and then allowed to cool at room temperature. The resulting crude solid was collected by filtration and dried at room temperature (Yield 88%). Suitable yellow crystals of the title compound for X-ray study were formed by slow evaporation of the solvent (methanol-chloroform, 1:1 v/v) over 3 days at room temperature. Anal. Calc. for C<sub>15</sub>H<sub>15</sub>NO<sub>3</sub>: C, 70.02; H, 5.88; N, 5.44%. Found: C, 70.28; H, 5.55; N, 5.71%. IR (KBr pellet, cm<sup>-1</sup>): 2860–3050 (m, C-H aromatic and aliphatic), 1627 (s, C=N), 1508–1560 (m, C=C aromatic). <sup>1</sup>H-NMR (CDCl<sub>3</sub>,  $\delta$ (ppm)): 3.92 (3Ha, s), 3.95 (3Ha, s), 6.92 (1Hd, q), 7.03 (2Hf, m), 7.16 (1Hc, d), 7.19 (1Hi, d), 7.29 (1Hb, s), 7.36 (1He, dd), 7.75 (1Hg, dd), 9.11 (1Hh, s).

# X-Ray Single Crystal Analysis

Crystallographic measurements were done with Rigaku RAXIS-RAPID II diffractometer, with graphite monochromataed Mo  $K\alpha$  radiation ( $\lambda = 0.71075$  Å) at 180 K. A numerical absorption correction was applied for the data [20]. The crystal structure of 1 was solved by direct methods using program SHELXS97 [21] and refined by full-matrix least-squares technique based on  $F^2$ . The C-bound H atoms were placed in geometrically idealized positions (C–H = 0.95 or 0.98 Å) and allowed to ride on their parent atoms, with  $U_{iso}(H) = 1.2U_{eq}(C)$  or  $1.5U_{eq}$ (methyl C). The O-bound H atom was located in a difference Fourier map and the positional parameters were refined, with  $U_{iso}(H) = 1.2U_{eq}(O)$ . Crystallographic data and details of the data collection and structure refinement are listed in Table 1. The molecular structure plots were prepared by ORTEP-3 [22].

 Table 1
 Crystallographic data and detail of the structure refinement for 1

Empirical formula	C <sub>15</sub> H <sub>15</sub> NO <sub>3</sub>
Formula weight	257.29
Crystal system	Monoclinic
Space group	C2/c
A (Å)	19.4581(13)
<i>b</i> (Å)	9.5805(5)
<i>c</i> (Å)	13.8431(7)
$\beta$ (deg)	93.471(2)
$V(\text{\AA}^3)$	2575.9(3)
Ζ	8
$\mu (\mathrm{mm}^{-1})$	0.09
T <sub>min</sub> , max	0.965, 0.980
Measured reflections	16393
Independent reflections	3751
Reflection with $I > 2\sigma(I)$	3345
Parameters	175
R <sub>int</sub>	0.023
$R[F^2 > 2\sigma(F^2)]$	0.041
$wR(F^2)$	0.129
$\Delta \rho_{\text{max, min}} (e \text{\AA}^{-3})$	0.35, -0.24

Theoretical Methods

The geometry of **1** has been optimized by using HF model with the method at 6-31G basis set. All HF calculations were performed using the Gaussian 98 R-A.9 package [23].

## **Results and Discussions**

Synthesis, FT-IR and <sup>1</sup>H-NMR Spectroscopy of (1)

The title compound **1** was prepared in yield of 88% by reaction of 2,5-dimethoxybenzaldehyde and 2-aminophenol in methanolic solution. It is air-stable in the solid state for about 3 months. The stability of dissolved compound is much shorter than in the solid state and depends on the

nature of the solvent. The title compound **1** is very slightly soluble in common organic solvents such as acetonitrile and methanol but completely soluble in chloroform and dichloromethane.

The <sup>1</sup>H-NMR spectrum of the title compound **1** was recorded using CDCl<sub>3</sub> as the solvent and data were summarized in the experimental section. The <sup>1</sup>H-NMR spectra of **1** is shown in Fig. 1. Three hydrogen atoms of the methoxy groups (**Ha**) have one signal in the 1H-NMR spectrum at 3.92 and 3.95 ppm. The hydrogen of azomethine group (**Hb**) was shown at  $\delta = 7.29$  ppm as a singlet. Aromatic ring protons of **1** are shown in the range  $\delta = 6.92$  ppm (1**Hd**),  $\delta = 7.03$  ppm (2**Hf**), 7.16 ppm (1**Hc**), 7.19 ppm (1**Hi**), 7.36 ppm (1**He**) and 7.75 ppm (1**Hg**). The hydrogen of hydroxy group (**Hh**) was shown at  $\delta = 9.11$  ppm as a singlet.

### X-Ray Crystal Structure of (1)

An ORTEP-3 view of the title compound 1 with the atom numbering scheme is given in Fig. 2. Selected bond lengths and angles are given in Table 2, along with the calculated bond parameters. All the bond lengths and angles in compound 1 are in the normal range [24].

The N1–C7 distance of 1.2892(12) Å is within the range of a double C=N bond, while the N1–C1 distance of 1.4254(12) Å is comparable to single C–N bond distances in other Schiff-base compounds [25–29].

The bond angles C8–C7–N1 and C7–N1–C1 are 124.95(9) and 117.22(8)°, respectively, and they are consistent with the  $sp^2$  hybrid character for C7 and N1 atoms [24–26]. The torsion angles in C6–C1–N1–C7 and





Fig. 2 An ORTEP-3 view of the title compound 1 shown with 35% displacement ellipsoids

C2–C1–N1–C7 are 47.15(13)° and -133.70(9)°, respectively, indicating the C1/N1/C7/C8 plane and the aromatic plane C1 to C6 ring are bent into each other. Then, in this compound the two substituted benzene rings are not coplanar and make a dihedral angle of 53.67(5)°. One methoxy group (O2–C14) lies in the C8–C13 benzene plane, with a torsion angle C14–O2–C9–C10 = -0.36(17)°, while the other group (O3–C15) is slightly twisted out the plane, with a torsion angle C15–O3–C12–C13 = -12.10(15)°. In the crystal structure, two molecules are stabilized by a pair of intermolecular O1–H1…N1<sup>i</sup> hydrogen bonds between hydroxy oxygen atom and imine nitrogen atom to form a dimeric unit (Fig. 3). The O1…N1<sup>i</sup> distance is 2.7223(11) Å



	Experimental	Theoretica
O1–C2	1.3559(12)	1.361
O2–C9	1.3648(13)	1.375
O2-C14	1.4275(15)	1.427
O3–C12	1.3749(13)	1.371
O3-C15	1.4249(14)	1.430
N1-C7	1.2892(12)	1.261
N1-C1	1.4254(12)	1.402
C7–C8	1.4617(13)	1.469
C9O2C14	117.15(10)	121.73
C12-O3-C15	116.95(8)	121.53
C7-N1-C1	117.22(8)	121.44
C6-C1-N1	121.74(9)	119.66
C2C1N1	119.02(8)	121.46
O1-C2-C3	117.25(9)	119.75
O1-C2-C1	123.52(9)	119.58
N1-C7-C8	124.95(9)	124.53
O2-C9-C10	123.41(10)	121.64
O2–C9–C8	116.60(9)	119.05
O3-C12-C13	124.93(9)	124.46
O3-C12-C11	115.25(9)	116.29

Table 2 Selected bond lengths (Å) and angles (°) for 1 by X-ray and theoretical calculations

<b>T</b> 11 <b>A</b>	<b>T</b> 1 1		1 1		0	c 4
Table 3	Experimental	hydrogen	bond	geometries (A	, ˘)	tor 1

D-H…A	D-H	H…A	$D \cdots A$	$D ext{-} ext{H} ext{-} ext{A}$
O1–H1…N1 <sup>i</sup>	0.896(16)	1.836(16)	2.7223(11)	169.9(15)
C6–H6…O3 <sup>ii</sup>	0.95	2.59	3.5270(14)	171

Symmetry codes: (i) -x + 1. y, -z + 1/2; (ii) -x + 1, -y, -z + 1Cg1 is the centroid of the benzene C1–C6 ring



**Fig. 3** A view of a dimeric structure of 1, formed by  $O1-H1\cdots N1^{i}$  hydrogen bonds [symmetry code: (i) -x + 1, y, -z + 1/2]

is clearly indicative of strong intermolecular hydrogen bonding because this distance is shorter than the sum of the van der Walls radii (3.07 Å) [30]. The dimeric units are further linked via C6–H6····O3<sup>ii</sup> hydrogen bond, forming a 1D chain running along the c axis (Fig. 4 and Table 3).



Fig. 4 Connected dimers of 1 viewed along the c axis showing the one-dimensional hydrogen bonds. The *dashed lines* represent the intermolecular C6–H6…O3 hydrogen bonds



Fig. 5 The structure and selected numbering of four conformers considered in the gas phase of 1

Table 4 Calculated total energy<sup>a</sup> of conformers A–D

	Α	В	С	D
DFT/6-31G	-855.402	-850.893	-850.978	-850.990

<sup>a</sup> Total energies in Hartree

## Computational Study

Molecular conformation obtained from HF calculation of **1** shows an agreement data (Bond distances and angles) between theoretical and experimental parameters. The calculated structural parameters are listed in Table 2. The

small differences between the theoretical and experimental parameters can be attributed to the fact that the HF calculations were carried out with isolated molecules in the gaseous phase whereas the X-ray parameters were based on molecules in the solid state. The single crystal X-ray diffraction study on this compound clearly indicates that the present compound exists in *trans* configuration around the C=N (Fig. 3). But, in the gas phase of the *trans* isomer the four conformers were found. Calculated *trans* conformers with selected numbering are shown in Fig. 5a.

Conformer **B** was obtained with rotation of  $\mathbf{R_1}$  ring (containing hydroxy group) around C1–N1 bond, while rotation of  $\mathbf{R_2}$  ring (containing methoxy groups) around C7–C8 yields the conformer **C**. But, rotations of  $\mathbf{R_1}$  and  $\mathbf{R_2}$ rings around the C1–N1 and C7–C8, respectively, yield the conformer **D** (Fig. 5). The results of calculated total energies and relative stabilities of these conformers are presented in Table 4. In consistent with results obtained in the solid state, theoretical studies predict that in the gas phase conformer **A** is the most stable, because the energy of this conformer is lower than the others.

### Conclusion

A new bidentate Schiff-base compound **1** has been synthesized and characterized by elemental analysis, FT-IR and <sup>1</sup>H-NMR spectroscopy. Its crystal structure was determined by single-crystal X-ray diffraction method. The molecular geometry of this compound has been analyzed by Gaussian (HF method) calculation. The observed molecular conformation of **1** from HF method calculation agrees well with that obtained from X-ray study.

# **Supplementary Data**

Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Center, CCDC No. 753756. 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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