

UDC 548.737:541.67

**CHARACTERIZATION OF SCHIFF BASES DERIVED FROM
3,4-DIMETHOXYBENZALDEHYDE: THE CRYSTAL STRUCTURE
OF N,N'-BIS(3,4-DIMETHOXYBENZYLIDENE)-2,2-DIMETHYLPROPANE-
1,3-DIAMINE HYDRATE**

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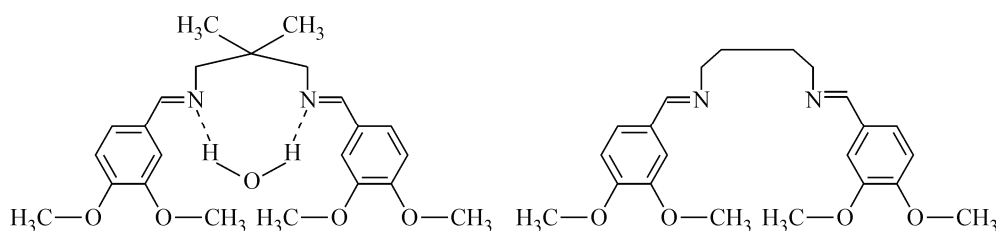
Received March, 4, 2012

The Schiff base compounds *N,N'*-bis(3,4-dimethoxybenzylidene)-2,2-dimethylpropane-1,3-diamine hydrate, (3,4-MeO-ba)₂Mepn.H₂O (**1**), and *N,N'*-bis(3,4-dimethoxybenzylidene)butane-1,4-diamine, (3,4-MeO-ba)₂bn (**2**), with different central groups derived from 3,4-dimethoxybenzaldehyde are synthesized and characterized by elemental analysis, FT-IR and ¹H NMR spectroscopy. The crystal structure of **1** is determined by single crystal X-ray diffraction. Each imino functional group (—C=N—) is coplanar with its adjacent benzene ring and the two benzene rings form a dihedral angle of 86.868(27)°. Title compound **1** crystallizes in the monoclinic space group *P2₁/n* with unit cell parameters: *a* = 9.0774(2) Å, *b* = 29.2138(5) Å, *c* = 8.5696(2) Å, β = 92.4756(14)°, *V* = 2270.41(8) Å³ and *Z* = 4.

Keywords: diimine, Schiff base, spectroscopy, single crystal X-ray diffraction.

INTRODUCTION

Schiff bases are widely used ligands in transition metal complexes and generally in inorganic chemistry [1, 2]. They have been found to exhibit biological activity [3—5] and photochromic properties [6]. They are prepared in a simple way by condensing a carbonyl group with an amine, usually in an alcohol solution [7, 8]. The most common examples of these compounds are prepared from salicylaldehyde derivatives to form a Schiff base ligand [9, 10]. Our group is interested in the synthesis, characterization and crystal structure of new Schiff base compounds and their transition metal complexes [11—14]. As a part of our ongoing studies, we report the synthesis and spectral characterization of Schiff bases prepared by the condensation of 3,4-dimethoxybenzaldehyde and two diamine derivatives (Scheme 1).



Scheme 1. Chemical structure of Schiff bases **1** (left) and **2** (right)

EXPERIMENTAL

Infrared spectra were recorded using KBr disks on a FT—IR Perkin—Elmer spectrophotometer. Elemental analyses were carried out using a Heraeus CHN-O-Rapid analyzer. ^1H NMR spectra were measured on a BRUKER DRX-500 AVANCE spectrometer at 500 MHz. All chemical shifts are reported in δ units downfield from TMS. All reagents and solvents for the synthesis and analysis were commercially available and used as received without further purifications.

General procedure for the synthesis of 1 and 2. 3,4-Dimethoxybenzaldehyde (0.4 mmol) and 2,2-dimethylpropane-1,3-diamine (0.2 mmol) or butane-1,4-diamine (0.2 mmol) were dissolved in a mixture of methanol:chloroform (1:1 v/v, 20 ml) at room temperature. The mixture was stirred and heated for 30 min to give a clear solution. After cooling the product was allowed to crystallize at room temperature. Colorless crystals were formed at the bottom of the vessel after 5 days of slow evaporation of the solvent. The resulting colorless crystals were collected by filtration and dried at room temperature.

Anal. Calc. for **1**, $\text{C}_{23}\text{H}_{30}\text{N}_2\text{O}_4 \cdot 0.59(\text{H}_2\text{O})$: C, 67.52; H, 7.68; N, 6.85 %. Found: C, 67.92; H, 7.65; N, 6.78 %. Yield: 83 %. IR (KBr pellet, cm^{-1}): 2922, 2960, 3008 (CH aliphatic and aromatic), 2837 (s, —CH=N—), 1639 (s, C=N), 1512, 1583, 1600 (C—C aromatic). ^1H NMR (500 MHz, CDCl_3 , δ (ppm)): 0.94 (s, 6H), 3.40 (s, 4H), 3.77 (s, 6H), 3.78 (s, 6H), 6.99 (d, 2H), 7.23 (dd, 2H), 7.37 (d, 2H), 8.18 (s, 2H).

Anal. Calc. for **2**, $\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_4$: C, 68.73; H, 7.34; N, 7.29 %. Found: C, 68.84; H, 7.45; N, 7.33 %. Yield: 83 %. IR (KBr pellet, cm^{-1}): 2912, 2937, 2972, 3000 (CH aliphatic and aromatic), 2865 (s, —CH=N—), 1638 (s, C=N), 1514, 1585, 1600 (C—C aromatic). ^1H NMR (500 MHz, CDCl_3 , δ (ppm)): 1.75 (q, 4H), 3.61 (t, 4H), 3.87 (s, 6H), 3.90 (s, 6H), 6.84 (d, 2H), 7.10 (dd, 2H), 7.39 (d, 2H), 8.16 (s, 2H).

X-ray structure determination. Single crystal with the dimensions $0.43 \times 0.30 \times 0.21$ mm of **1** was chosen for the X-ray diffraction study. Crystallographic measurements were performed at 120 K with a four circle Gemini CCD diffractometer (Oxford diffraction, Ltd.) with mirrors-collimated $\text{CuK}\alpha$ radiation ($\lambda = 1.54184 \text{ \AA}$). The crystal structures were solved by direct methods with the SIR2002 program [15] and refined with the Jana2006 program package [16] by the full-matrix least-squares technique on F^2 . The molecular structure plots were prepared by ORTEP III [17]. Hydrogen atoms were mostly discernible in difference Fourier maps and could be refined to reasonable geometry. According to common practice they were nevertheless kept in ideal positions during the refinement. The isotropic atomic displacement parameters of hydrogen atoms were evaluated as $1.2U_{\text{eq}}$ of the parent atom. Crystallographic data and details of the data collection and structure solution and refinements are listed in Table 1.

Table 1

Crystallographic data collection and structure refinement parameters of **1**

Chemical formula	$\text{C}_{23}\text{H}_{30}\text{N}_2\text{O}_4 \cdot 0.59(\text{H}_2\text{O})$	$R[F^2 > 2\sigma(F^2)]$	0.034
Crystal system	Monoclinic	Parameters	278
T , K	120	Space Group	$P2_1/n$
a , b , c , \AA	9.0774(2), 8.5696(2), 29.2138(5)	Measured / Independent reflections	30708 / 3589
β , deg.	92.4756(14)	Reflection with $I > 3\sigma(I)$	3265
V , \AA^3 ; Z	2270.41(8); 4	S	2.40
μ , mm^{-1}	0.68	$wR(F^2)$	0.112
$T_{\text{max}} / T_{\text{min}}$	0.873 / 0.687	Crystal size, mm	$0.43 \times 0.30 \times 0.21$
R_{int}	0.024	$\Delta\rho_{\text{max}} / \Delta\rho_{\text{min}}$, $\text{e}/\text{\AA}^{-3}$	0.16 / -0.13

RESULTS AND DISCUSSION

The two Schiff base compounds (3,4-MeO-ba)₂Mepn (**1**) and (3,4-MeO-ba)₂bn (**2**), interesting as potentially bidentate ligands, were cleanly synthesized in a methanol solution and >85 % yield. The stability of dissolved compounds is much shorter than that in the solid state and depends on the nature of the solvent. The title compounds are stable at room temperature in methanol, ethanol, and acetonitrile for 5 days, and also remain unchanged in chloroform and dichloromethane for about 2 days [11].

The expected chemical structures of these compounds are supported from their FT—IR spectra by the absence of the carbonyl and primary amine groups of the reagents, and the presence of a Schiff base band at 1639 cm⁻¹ in **1** and 1638 cm⁻¹ in **2** [11, 12]. The FT—IR spectra of **1** and **2** also show several bands corresponding to aromatic and aliphatic C—H stretching (2837 cm⁻¹, 2922 cm⁻¹, 2960 cm⁻¹, and 3009 cm⁻¹ for **1** and 2865 cm⁻¹, 2912 cm⁻¹, 2937 cm⁻¹, 2972 cm⁻¹, 3001 cm⁻¹, and 3019 cm⁻¹ for **2**) and aromatic C—C stretching (1512 cm⁻¹, 1584 cm⁻¹, and 1600 cm⁻¹ for **1** and 1514 cm⁻¹, 1585 cm⁻¹, and 1600 cm⁻¹ for **2**).

Both Schiff bases have simple and similar ¹H NMR spectra in the CD₃Cl solution [Figs. 1 and 2 respectively]. The CH₃O— protons are observed as two singlet signals at 3.77 ppm and 3.78 ppm for **1**

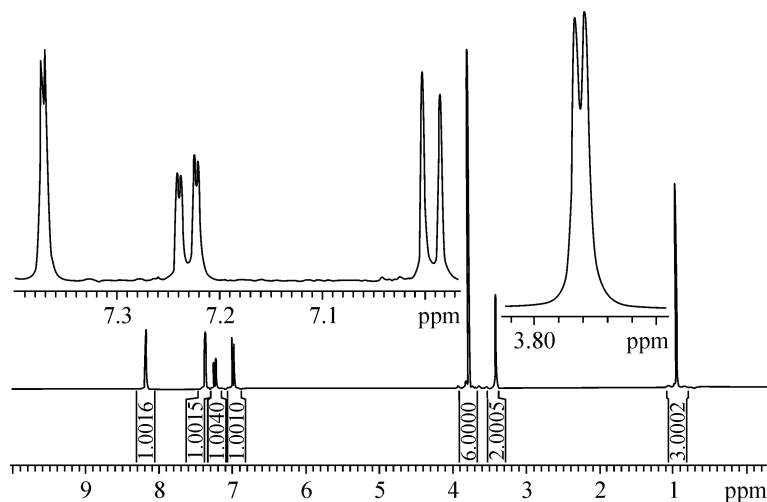


Fig. 1. ¹H NMR spectra of **1**

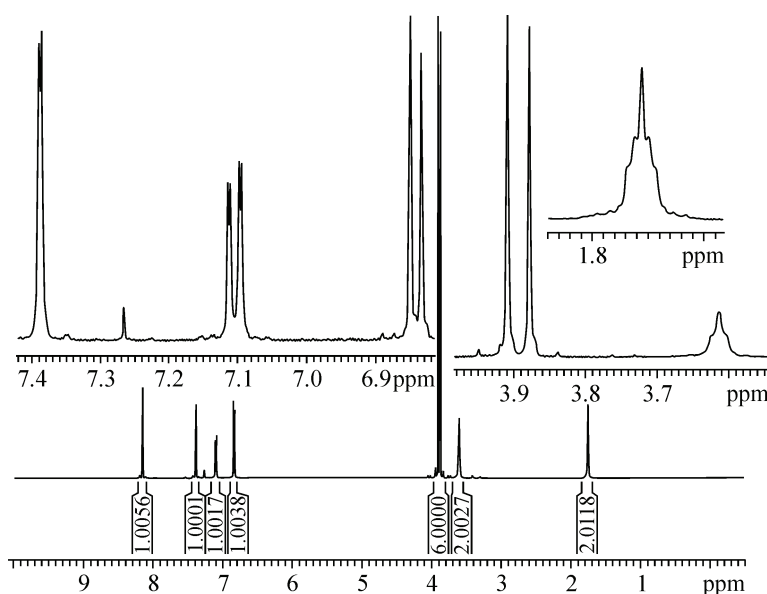
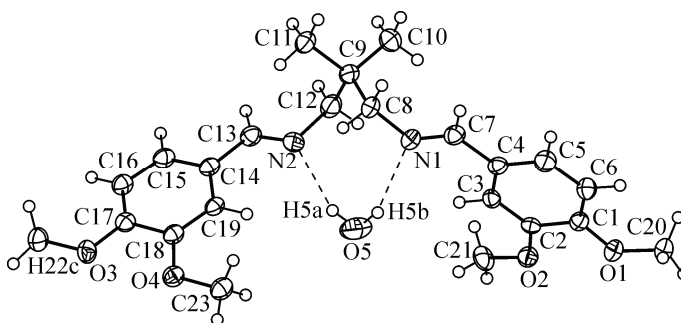


Fig. 2. ¹H NMR spectra of **2**

Fig. 3. Molecule of **1** with the atom numbering scheme. Displacement ellipsoids are drawn at the 50 % probability level. The O—H···N hydrogen bonds are drawn as dotted lines



and at 3.87 ppm and 3.90 ppm for **2**. The CH₃ protons are observed as a singlet at 0.94 ppm for **1**. The CH₂ protons are observed as a singlet at 3.34 ppm for **1** and as a triplet signal at 3.61 ppm and a quintet signal at 1.75 ppm for **2**.

The aromatic hydrogens are observed as a doublet at 6.99 ppm for **1** and 6.84 ppm for **2**, as a doublet of a doublet at 7.23 ppm for **1** and 7.10 ppm for **2** and as a doublet at 7.37 ppm for **1** and 7.38 ppm for **2**. The azomethine protons of **1** and **2** are observed as a singlet signal at 8.18 ppm for **1** and 8.16 ppm for **2**.

Crystal structure of 1. Only the molecular structure for compound **1** was determined by single crystal X-ray diffraction (Fig. 3). We failed to prepare a suitable single crystal of **2**. Compound **1** crystallizes in the monoclinic space group $P2_1/n$ and is non-planar, with a dihedral angle between the two aromatic rings of 86.868(27)°. In the crystal structure of **1**, the water molecule is connected to the Schiff base by two O—H···N hydrogen bonds. The molecule adopts an *E* configuration about the N1=C7 and N2=C13 bonds with the azomethine nitrogen atoms [18]. The bond lengths and angles of **1** are very close to the corresponding ones found in Cambridge Structural Database [11–14, 19]. Bond lengths and angles within the aromatic rings are consistent with those expected for sp^2 aromatic carbon atoms. The lengths of C4—C7 and C13—C14 (1.4645(16) Å and 1.4660(17) Å respectively) are consistent with the length of single bonds between sp^2 -hybridized carbon atoms while the lengths in azomethine groups (N1=C7 1.2703(15) Å and N2=C13 1.6677(13) Å) are close to the value for a double bond [11–14]. The C7—N1—C8, C12—N2—C13, N1—C7—C4, and N2—C13—C14 bond angles are 118.61(10)°, 118.27(11)°, 122.80(10)°, and 122.89(14)° respectively, which is consistent with the sp^2 -hybridized nitrogen (N1 and N2) and carbon (C7 and C13) atoms. The two 3,4-dimethoxybenzylidene groups are bridged by the —CH₂—C(CH₃)₂—CH₂— fragment via two C=N double bonds (Fig. 3), with the C4···C14 distances between aromatic rings being ca 7.9211(16) Å.

CONCLUSIONS

In this work, we report two Schiff base compounds (3,4-MeO-ba)₂Mepn·H₂O (**1**) and (3,4-MeO-ba)₂bn (**2**) with different central groups. Elemental analyses confirm the chemical composition of the synthesized compounds, while FT—IR and ¹H NMR spectroscopy confirms the functional groups, particularly —HC=N— and aromatic groups, of the compounds. In the crystal structure of **1**, the water molecule is connected to the Schiff base by two O—H···N hydrogen bonds.

Acknowledgements. We acknowledge the Golestan University (GU) and Qaemshahr Branch, Islamic Azad University for partial support of this work, the Institutional Research Plan No. AVOZ10100521 of the Institute of Physics ASCR, v.v.i. Na Slovance 2, 18221 Prague 8, Czech Republic.

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