

Short communication

Synthesis and Characterization of Two Diimine Schiff Bases Derived from 2,4-Dimethoxybenzaldehyde: The Crystal Structure of *N,N'*-Bis(2,4-dimethoxybenzylidene)-1,2-diaminoethane

Aliakbar Dehno Khalaji^{1,*} Karla Fejfarova² and Michal Dusek²

¹ Department of Chemistry, Faculty of Science, Golestan University, Gorgan, Iran

² Institute of Physics of the ASCR, v.v.i., Na Slovance 2, 182 21 Prague 8, Czech Republic

* Corresponding author: E-mail: alidkhalaji@yahoo.com
Tel/fax.: +98 171 4427050

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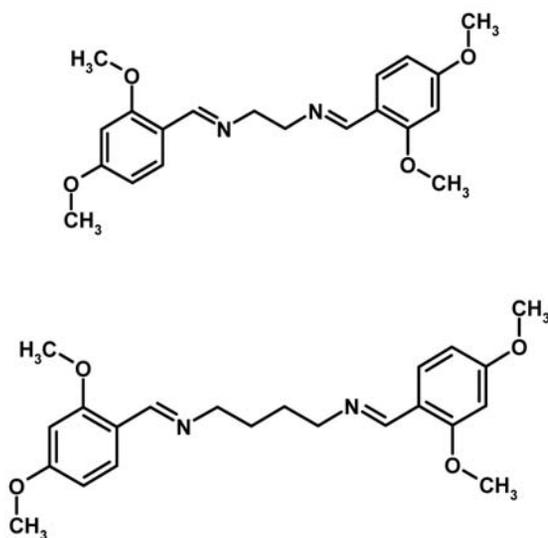
Abstract

Two diimine Schiff bases derived from 2,4-dimethoxybenzaldehyde; *N,N'*-bis(2,4-dimethoxybenzylidene)-1,2-diaminoethane (**1**) and *N,N'*-bis(2,4-dimethoxybenzylidene)-1,4-diaminobutane (**2**), were prepared and characterized by elemental analyses, FT-IR and ¹H NMR spectroscopy. The crystal structure of **1** has been determined by single crystal X-ray diffraction. Its molecule adopts an *E* configuration with respect to the C=N bond and is located on a center of inversion with one half-molecule in the asymmetric unit.

Keywords: Diimine Schiff bases; FT-IR; ¹H-NMR spectroscopy; crystal structure; X-ray diffraction.

1. Introduction

N-substituted imines, also known as Schiff bases, have been extensively studied as ligands in the development of coordination compounds of transition metals complexes. In that time they have become one of the most typical ligands in coordination chemistry.^{1–5} These complexes have been highlighted in coordination chemistry where they are used as catalysts for organic reactions^{6,7} and they also have interesting magnetic properties.^{8–10} In the previous works, we reported the synthesis and crystal structure of different Schiff-base compounds^{11–15} and their transition metal complexes.^{16–20} In this work, we report on preparation and characterization of two Schiff bases; *N,N'*-bis-(2,4-dimethoxybenzylidene)-1,2-diaminoethane (**1**) and *N,N'*-bis-(2,3-dimethoxybenzylidene)-1,4-diaminobutane (**2**) (Scheme 1). Both compounds were characterized by elemental analyses, FT-IR, UV-Vis and ¹H-NMR spectroscopy. Molecular structure was also determined by single-crystal X-ray diffraction for compound **1**, whereas we could not get suitable crystals for compound **2**.



Scheme 1. The Schiff bases *N,N'*-bis-(2,4-dimethoxybenzylidene)-1,2-diaminoethane (**1**) (top) and *N,N'*-bis-(2,4-dimethoxybenzylidene)-1,4-diaminobutane (**2**) (bottom).

2. Experimental

All reagents and solvents for synthesis and analysis were commercially available and used as received without further purification. Elemental analyses were carried out using a Heraeus CHN-O-Rapid analyzer. ^1H NMR spectra were measured with a BRUKER DRX-500 AVANCE spectrometer at 500 MHz and all chemical shifts are reported in δ units downfield from TMS. The infrared spectra were recorded on a JASCO 680 plus FT-IR spectrophotometer as a KBr pellet.

2.1. Preparation of **1** and **2**

2,4-dimethoxybenzaldehyde (0.4 mmol) and corresponding amines (0.2 mmol) were dissolved in methanol (25 ml) at room temperature. The mixture was stirred and heated for 20 min to give a clear solution. After keeping the solution in air for 3 days by slow evaporation of the solvent, colorless crystals were formed at the bottom of the vessel. The resulting colorless crystals were collected by filtration and dried at room temperature.

Compound 1. [Reactant materials: 2,4-dimethoxybenzaldehyde, 1,2-diaminoethane] Colorless crystals. Yield: 91%. *Anal.* Calc. for $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_4$: C, 67.40; H, 6.79; N, 7.86%. Found: C, 67.45; H, 6.84; N, 7.90%. IR (KBr pellet), ν (cm^{-1}) 2832–3001 (m, C–H aromatic and aliphatic), 1637 (s, C=N), 1511–1559 (C=C aromatic). ^1H NMR (CDCl_3), δ (ppm) 3.78 (s, 6H, ortho $\text{CH}_3\text{--O}$), 3.80 (s, 6H, para $\text{CH}_3\text{--O}$), 3.89 (s, 4H, $\text{--CH}_2\text{--CH}_2\text{--}$), 6.38 (d, 2H, **H** meta), 6.48 (dd, 2H, **H** meta), 7.87 (d, 2H, **H** ortho), 8.60 (s, 2H, --HC=N).

Compound 2. [Reactant materials: 2,4-dimethoxybenzaldehyde, 1,4-diaminoethane] Colorless crystals. Yield: 88%. *Anal.* Calc. for $\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_4$: C, 68.73; H, 7.34; N, 7.29%. Found: C, 68.77; H, 7.39; N, 7.35%. IR (KBr pellet), ν (cm^{-1}) 2811–2990 (m, C–H aromatic and aliphatic), 1639 (s, C=N), 1499–1605 (C=C aromatic). ^1H NMR (CDCl_3), δ (ppm) 1.73 (q, 4H, C– $\text{CH}_2\text{--CH}_2\text{--C}$), 3.60 (t, 4H, $\text{--N--CH}_2\text{--}$), 3.80 (s, 6H, ortho $\text{CH}_3\text{--O}$), 3.81 (s, 6H, para $\text{CH}_3\text{--O}$), 6.40 (d, 2H, **H** meta), 6.49 (dd, 2H, **H** meta), 7.87 (d, 2H, **H** ortho), 8.54 (s, 2H, --HC=N).

2.2. X-ray Structure Determination

A single crystal of **1** with the dimensions 0.44 mm \times 0.23 mm \times 0.13 mm was chosen for X-ray diffraction study. Crystallographic measurements were performed at 120K with four circle CCD Oxford Gemini diffractometer, with mirrors-collimated Cu $K\alpha$ radiation ($\lambda = 1.54184 \text{ \AA}$). The crystal structure was solved by direct methods with program SIR2002²¹ and refined with the Jana2006 program package²² by full-matrix least-squares technique on F^2 . The molecular structure plots were prepared by ORTEP III.²³ Hydrogen atoms were mostly discernible in difference Fourier maps and could be refined to reasonab-

le 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 refinements are listed in Table 1.

3. Results and Discussion

3.1. Synthesis and Spectroscopy

Both compounds **1** and **2** were obtained in relatively high yields, 91% and 88% respectively. The stability of dissolved compounds is much shorter than in the solid state and depends on the nature of the solvent. The title compounds are stable in methanol and acetonitrile solution at room temperature for about 8 days and at 273 K for 15 days. They also remain unchanged in chloroform and dichloromethane for about 1 day at room temperature and for 3 days at 273 K. The title compounds are very slightly soluble in common organic solvents such as acetonitrile and methanol; however, they are completely soluble in chloroform and dichloromethane.

Table 1. General data and the summary of X-ray experimental and structural details for compound **1**.

Empirical formula	$\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_4$
Formula weight	356.4
Crystal system	Monoclinic
Space group	$P2_1/n$
T (K)	120
a (\AA)	13.5120(7)
b (\AA)	14.8815(10)
c (\AA)	4.5132(3)
β (deg)	92.690(5)
V (\AA^3)	906.51(10)
Z	2
μ (mm^{-1})	0.75
T_{min}	0.764
T_{max}	0.908
Measured reflections	7001
Independent reflections	1416
Reflection with $I > 3\sigma(I)$	1037
R_{int}	0.035
S	1.35
$R[F^2 > 3\sigma(F^2)]$	0.035
$wR(F^2)$	0.088
Parameters	118
$\Delta\rho_{\text{max}}$ ($\text{e}\text{\AA}^{-3}$)	0.14
$\Delta\rho_{\text{min}}$ ($\text{e}\text{\AA}^{-3}$)	-0.14
Crystal size (mm^3)	$0.44 \times 0.23 \times 0.13$
Index ranges	$-15 \leq h \leq 15$ $-17 \leq k \leq 17$ $-5 \leq l \leq 5$

The strong bands at 1637 cm^{-1} for **1** and 1639 cm^{-1} for **2** in their respective FT-IR spectra are assigned to the C=N stretching vibration.²⁴ The FT-IR spectra of **1** and **2**

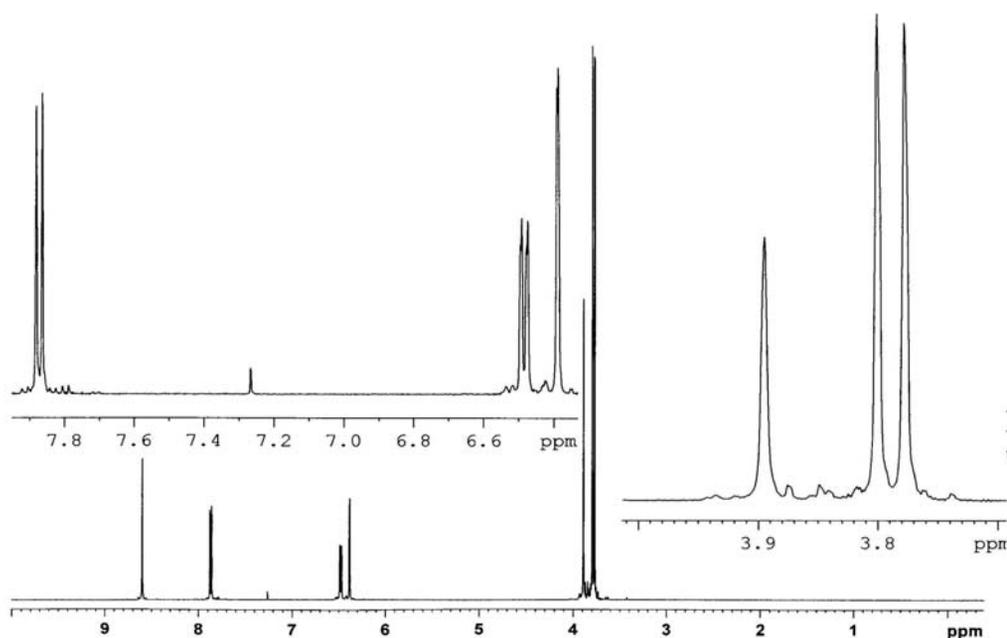


Figure 1. $^1\text{H-NMR}$ spectra of **1**.

also shows several weak bands corresponding to aromatic and aliphatic C-H stretching (2832 , 2850 , 2860 , 2893 , 2912 , 2945 , 2970 and 3001 cm^{-1} for **1** and 2811 , 2832 , 2865 , 2888 , 2940 , 2964 , 2990 and 3005 cm^{-1} for **2**), and aromatic C-C stretching (1511 , 1583 , 1599 and 1599 cm^{-1} for **1** and 1499 , 1561 , 1576 , 1605 cm^{-1} for **2**).²⁴

The ^1H NMR spectra of *N,N'*-bis-(2,4-dimethoxybenzylidene)-1,2-diaminoethane and *N,N'*-bis-(2,4-dimethoxybenzylidene)-1,4-diaminobutane are shown in

Figures 1 and 2, respectively. The spectrum for compound **1** display two singlet signals at 3.78 and 3.80 ppm, which are assigned to protons of the $\text{CH}_3\text{-O}$ - groups, and one singlet signal at 3.89 ppm assigned to protons of the $-\text{CH}_2\text{-CH}_2-$ group. The signal at 6.38 ppm and doublet signal at 6.48 ppm were assigned to aromatic *meta* protons, while the doublet signal at 7.87 belongs to aromatic *ortho* protons. The singlet signal at 8.60 ppm was assigned to $-\text{HC}=\text{N}$ group. The ^1H NMR spectra of compound **2** dis-

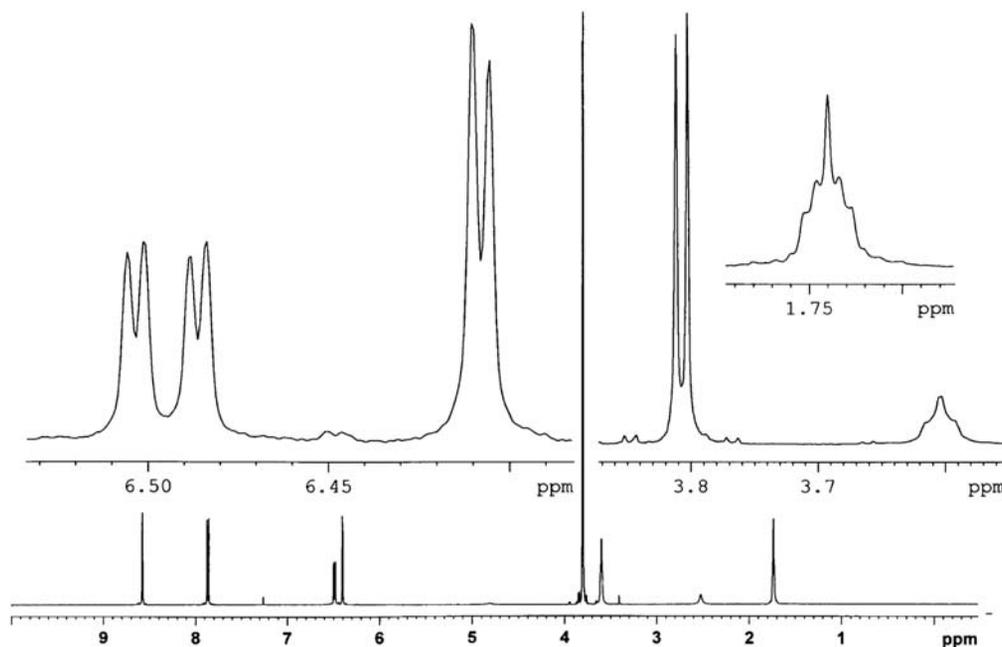


Figure 2. $^1\text{H-NMR}$ spectra of **2**.

play one quintet signal at 1.73 ppm assigned to protons of the $-\text{C}-\text{CH}_2-\text{CH}_2-\text{C}-$ group, one triplet signal at 3.60 ppm assigned to protons of $-\text{CH}_2-\text{N}=\text{}$ groups, and two singlet signals at 3.80 and 3.81 ppm which are assigned to protons of the $\text{CH}_3-\text{O}-$ groups. The signal at 6.40 ppm and dublet signal at 6.49 ppm were assigned to aromatic *meta* protons, while the doublet signal at 7.87 belongs to aromatic *ortho* protons. The singlet signal at 8.54 ppm was assigned to $-\text{HC}=\text{N}$ group.

3. 2. Crystal Structure of 1

Compound **1** crystallizes in the centrosymmetric space group $P2_1/n$. The molecule $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_4$ has a centre of symmetry with one half-molecule in the asymmetric unit. The molecular structure of compound **1** with the atom numbering scheme is given in Figure 3. All bond distances and angles are normal and are in good agreement with those reported in similar Schiff-base compounds.^{12–15,24} The C(7)-N(1) bond length of 1.2713(19) Å is close to the value for a double bond, while the C(8)-N(1) bond length of 1.454(2) Å is close to the value for a single bond, like in similar Schiff bases.^{12–15,24} The bond angles for atoms C(6)-C(7)-N(1) and C(7)-N(1)-C(8) are 122.47(14)° and 116.53(13)°, respectively, which is consistent with the sp^2 hybrid character of C(7) and N(1) atoms. The two 2,4-dimethoxybenzylidene groups are bridged by the $-\text{CH}_2-\text{CH}_2-$ fragment *via* two C=N double bonds (Figure 3), with the distance between aromatic rings, C(6)...C(6i), of *ca* 8.299 Å.

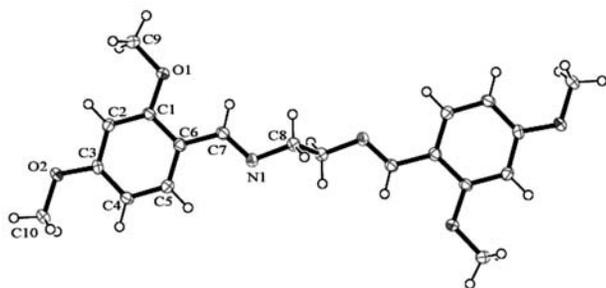


Figure 3. Molecule of **1**, showing the crystallographic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radius.

4. Conclusions

Two new Schiff bases were synthesized and crystal and molecular structure of compound **1** was successfully characterized. Elemental analyses confirms the chemical composition of the synthesized compounds while FT-IR and $^1\text{H-NMR}$ spectroscopy confirms the functional groups, particularly $-\text{HC}=\text{N}$ imine groups, of the compounds. The compound **1** has a centre of symmetry with one half-molecule in the asymmetric unit.

5. Acknowledgements

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Appendix A. Supplementary data

Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited at the Cambridge Crystallographic Center, CCDC No. 733842. Copies of the data can be obtained free of charge on <http://www.ccdc.cam.ac.uk>.

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Povzetek

Avtorji v prispevku poročajo o pripravi dveh Schiffovih baz; *N,N'*-bis(2,4-dimetoksibenziliden)-1,2-diaminoetana (**1**) in *N,N'*-bis(2,4-dimetoksibenziliden)-1,4-diaminobutana (**2**), pripravljenih iz 2,4-dimetoksibenzaldehida. Spojine so okarakterizirane s pomočjo elementne analize, FT-IR in ¹H NMR spektroskopije. Za spojino **1** je bila določena kristalna struktura iz katere je razvidno, da je molekula v *E* konfiguraciji z ozirom na C=N vez, ki je locirana v centru inverzije tako, da je polovica molekule v eni asimetrični enoti.