



## Short Communication

# Preparation and Crystal Structure of *N,N'*-bis(2,4-dimethoxybenzylidene)-butane-1,4-diamine Monohydrate



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### KEYWORDS

Schiff-base

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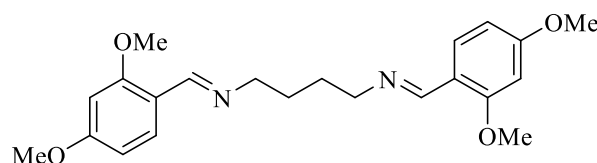
### ABSTRACT

In this work, the Schiff-base compound *N,N'*-bis(2,4-dimethoxybenzylidene)-butane-1,4-diamine monohydrate ((2,4-MeO-ba)<sub>2</sub>bn/H<sub>2</sub>O) was prepared by the condensation reaction of 2,4-dimethoxybenzaldehyde with butane-1,4-diamine in methanol solution and crystallizes as the monohydrate. The crystal structure of (2,4-MeO-ba)<sub>2</sub>bn/H<sub>2</sub>O (**1**) was determined using the X-ray diffraction (XRD) analysis. The compound crystallized in the monoclinic space group *C2/c*, with *a*=14.7116 (10), *b*=15.7333 (9), *c*=10.2013 (6) Å,  $\beta$ =112.704 (2)° and *Z*=4. There are one half-molecule and one half of a water molecule in the asymmetric unit, with the (2,4-MeO-ba)<sub>2</sub>bn molecule completed by inversion symmetry on the midpoint of the central C-C bond of the butane unit and the O atom of the water molecule situated on a twofold rotation axis. Within the imine functionality, the N-C bond lengths of 1.2643 (19) and 1.457 (2) Å were double and single bonds, respectively. Hydrogen bonds of the type O-H...N between the water molecule and the imine nitrogen atom of the (2,4-MeO-ba)<sub>2</sub>bn molecules led to formation of the layers propagating parallel to (100). The <sup>1</sup>H-NMR and FT-IR results confirmed the preparation of this ligand, as well.

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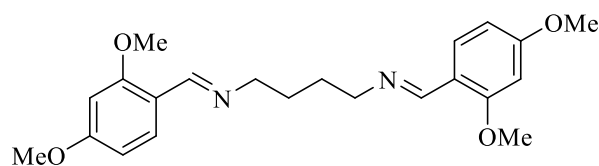
## Graphical Abstract



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## Introduction

Azomethines contain imine groups (CH=N) and discovered by the German chemist Hugo Schiff in 1864 [1]. This family of compounds are also denoted as Schiff-bases. Great research interest has been developed due to their different applications in various areas with respect to the nonlinear optical behaviour [2, 3], antimicrobial activity [4-6], and as anion sensors [7]. These compounds are prepared from the reaction of a carbonyl group (aldehyde or ketone) with an amine, usually in an alcohol solution [8-14]. For example, Dalapathi *et al.* [12] prepared  $N_2O_2$  Schiff-bases in methanolic solution and reported the anion receptor of them [12]. Recently, some Schiff-bases have been reported as effective corrosion inhibitors for metals in acid media [13, 14]. Based on these properties we have become interested in various Schiff-base compounds and their metal complexes [8-11]. For example, macrocyclic  $N_2O_2$  Schiff-bases prepared for condensing of a dialdehyde and diamine [15, 16]. Novel bis-NO acyclic Schiff-base have been reported, as well [17]. As a continuation of our previous works [8-11, 15-17], in this research study, the hydrated Schiff-base (2,4-MeO-ba)<sub>2</sub>bn/H<sub>2</sub>O was synthesized (Scheme 1) and characterized using the FT-IR and <sup>1</sup>H-NMR spectroscopy and X-ray crystallography.



**Scheme 1.** Chemical structures of (2,4-MeO-ba)<sub>2</sub>bn/H<sub>2</sub>O

## Experimental

### Materials and methods

All reagents and solvents for synthesis and analysis were commercially available and used as received without further purification. Elemental analysis (CHN) were carried out using a Heraeus CHN-O-Rapid analyser.

### Synthesis of (2,4-MeO-ba)<sub>2</sub>bn/H<sub>2</sub>O

2,4-dimethoxybenzaldehyde (0.4 mmol) and 1,4-diaminoethane (0.2 mmol) dissolve in methanol (25 mL) at room temperature. The mixture was stirred and heated for 20 min to prepare a clear solution. After keeping the solution under atmospheric conditions for 3 days by slow evaporation of the solvent, colourless crystals form at the bottom of the vessel. The crystals are collected by filtration and dried at

room temperature. Yield: 88%. Anal. Calc. for  $C_{22}H_{28}N_2O_4$ : C, 68.73, H, 7.34, N, 7.29%. Found: C, 68.77, H, 7.39, N, 7.35%. IR (KBr pellet,  $cm^{-1}$ ): 2811-2990 (m, C-H aromatic and aliphatic), 1639 (s, C=N), 1499-1605 (C=C aromatic).  $^1H$ -NMR ( $CDCl_3$ ,  $\delta$  (ppm)): 1.73 (q, 4H, C-CH<sub>2</sub>-CH<sub>2</sub>-C), 3.60 (t, 4H, -N-CH<sub>2</sub>-), 3.80 (s, 6H, *ortho* CH<sub>3</sub>-O-), 3.81 (s, 6H, *para* CH<sub>3</sub>-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).

### X-ray crystallography

A light-yellow single crystal of  $(2,4\text{-MeO-ba})_2bn/H_2O$  with dimensions 0.36×0.36×0.30 mm was selected for X-ray diffraction studies. Intensity data collections were performed with Mo  $K\alpha$  radiation ( $\lambda=0.71073 \text{ \AA}$ ) at room temperature on an APEXII four-circle CCD diffractometer (Bruker-AXS). Crystal structure easily solved by charge flipping with program SUPERFLIP [18], and refined with the Jana2006 program package [19] by full-matrix least-squares technique on  $F^2$ . The molecular structure plot prepared by Diamond 4.0 [20]. Hydrogen atoms are positioned geometrically (C-H=0.93 and 0.96  $\text{\AA}$ ) and refined as riding, with  $U_{iso}(H)=1.2 U_{eq}(C)$  and 1.5  $U_{eq}$  (methyl C), allowing for free rotation of the methyl groups. The H atom of the water molecule is found from a difference map and refined with an O---H distance restraints of 0.95  $\text{\AA}$  and  $U_{iso}(H)=1.2 U_{eq}(O)$ . Structure data and details of the data collections and structure refinements are listed in Table 1.

**Table 1.** Crystallographic data of  $(2,4\text{-MeO-ba})_2bn/H_2O$

Empirical formula, Formula weight	$C_{22}H_{28}N_2O_4 \cdot H_2O$ , 402.48
Crystal system, Space group	Monoclinic, $C2/c$
a ( $\text{\AA}$ )	14.7116(10)
b ( $\text{\AA}$ )	15.7333(9)
c ( $\text{\AA}$ )	10.2013(6)
$\beta$ (deg)	112.704(2)
V ( $\text{\AA}^3$ )	2178.2(2)
Z	4
$D_x$ ( $g/cm^3$ )	1.227
$\mu$ ( $mm^{-1}$ )	0.09
$\theta_{min}, \theta_{max}$	2.6, 26
$T_{min}, T_{max}$	0.969, 0.974
Measured, Independent reflections	13495, 2149
Reflection with $I > 2\sigma(I)$	1653
Parameters	138
$R_{int}$	0.027
S, $F_{000}$	1.07, 864
R [ $F^2 > 2\sigma(F^2)$ ], $W_r(F^2)$	0.039, 0.116
$\Delta\rho_{max}, \Delta\rho_{min}$ ( $e\text{\AA}^{-3}$ )	0.20, -0.16

Crystallographic data (excluding structure factors) for the structure reported in this study were deposited with the Cambridge Crystallographic Center, CCDC No. 772108. 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>.

## Results and discussion

Schiff-base compound (2,4-MeO-ba)<sub>2</sub>bn/H<sub>2</sub>O was prepared. FT-IR spectrum of this compound revealed several peaks for C-H, C=N and C=C vibrations. The sharp peak that appeared at 1639 cm<sup>-1</sup> assigned to the presence of C=N group and confirmed the preparation of compound. In the <sup>1</sup>H-NMR spectrum, the iminic protons (-HC=N-) appears at 8.54 ppm as singlet signal. Aromatic and aliphatic protons appeared at 6.40-7.87 ppm and 1.73-3.81 ppm, respectively. Compound (2,4-MeO-ba)<sub>2</sub>bn/H<sub>2</sub>O crystallizes in the centrosymmetric space group *C2/c*. The molecule C<sub>22</sub>H<sub>28</sub>N<sub>2</sub>O<sub>4</sub> located at the centre of symmetry with one half-molecule in the asymmetric unit. The molecular structure of compound (2,4-MeO-ba)<sub>2</sub>bn/H<sub>2</sub>O with the atom numbering scheme is presented in Figure 1. All the bond lengths and angles were found to be normal (Table 2) and in good agreement with those reported in similar Schiff-base compounds [9, 21, 22].

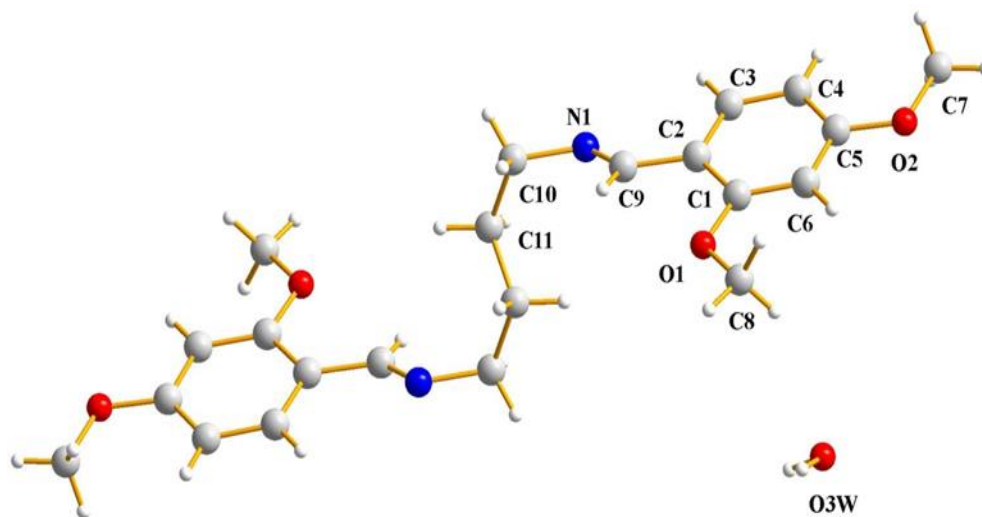
**Table 2.** Selected bond lengths (Å) and angles (°) of (2,4-MeO-ba)<sub>2</sub>bn·H<sub>2</sub>O

O1-C1	1.3636 (17)	C6-C1	1.373 (2)
O1-C8	1.417 (2)	N1-C10	1.457 (2)
C9-N1	1.2643 (19)	C2-C3	1.384 (2)
C9-C2	1.459 (2)	C2-C1	1.406 (2)
O2-C5	1.3670 (18)	C4-C3	1.378 (2)
O2-C7	1.419 (2)	C1-C10	1.515 (2)
C5-C6	1.383 (2)	C1-C11 <sup>i</sup>	1.519 (3)
C5-C4	1.383 (2)	O3W-H1W	0.95 (2)
C1-O1-C8	117.87 (13)	C3-C2-C9	121.82 (13)
N1-C9-C2	124.04 (14)	C1-C2-C9	120.62 (13)
C5-O2-C7	117.52 (12)	O1-C1-C6	124.1 (13)
O2-C5-C6	114.89 (13)	O1-C1-C2	115.35 (13)
O2-C5-C4	124.54 (14)	C6-C1-C2	120.60 (13)
C6-C5-C4	120.57 (14)	C3-C4-C5	118.50 (14)
C9-N1-C10	117.27 (14)	C4-C3-C2	122.68 (14)
C1-C6-C5	120.21 (13)	C10-C11-C11 <sup>i</sup>	113.45 (16)
C3-C2-C1	117.44 (14)	N1-C10-C11	111.44 (13)

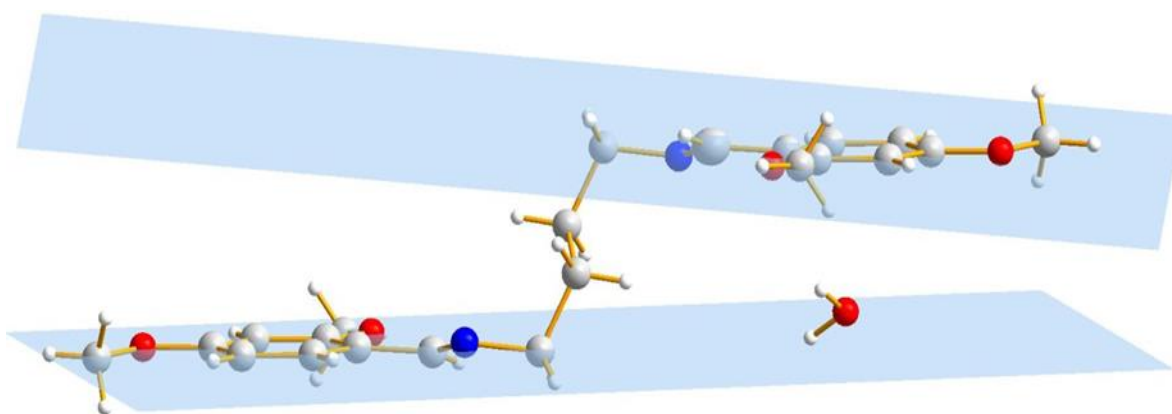
Symmetry codes: (i)  $-x, -y, -z+2$

The C9=N1 bond length of 1.2643 (19) Å conformed to the value for a double bond, while the C10-N1 bond length of 1.457 (2) Å conformed to the value for a single bond, similar to that of Schiff-base

compounds [9-14]. The bond angles C10-N1-C9 and N1-C9-C2 bond angles were 117.27 (14) and 124.04 (14)°, respectively, which was consistent with the  $sp^2$  hybrid character of N1 and C9 atoms. In this compound, the methoxy groups, the phenyl ring and the iminic C=N bond are on a plane, so that the two sides of the ligand are quite flat. The two planes were not parallel and perpendicular to the plane resulting from the carbons of the butane group (Figure 2). The C2...C2' distances between aromatic rings is 9.004 Å and is larger than this distance in similar compound (3,4-MeO-ba)<sub>2</sub>Mepn/H<sub>2</sub>O [21].



**Figure 1.** Molecular structure of the title compound, showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted for clarity

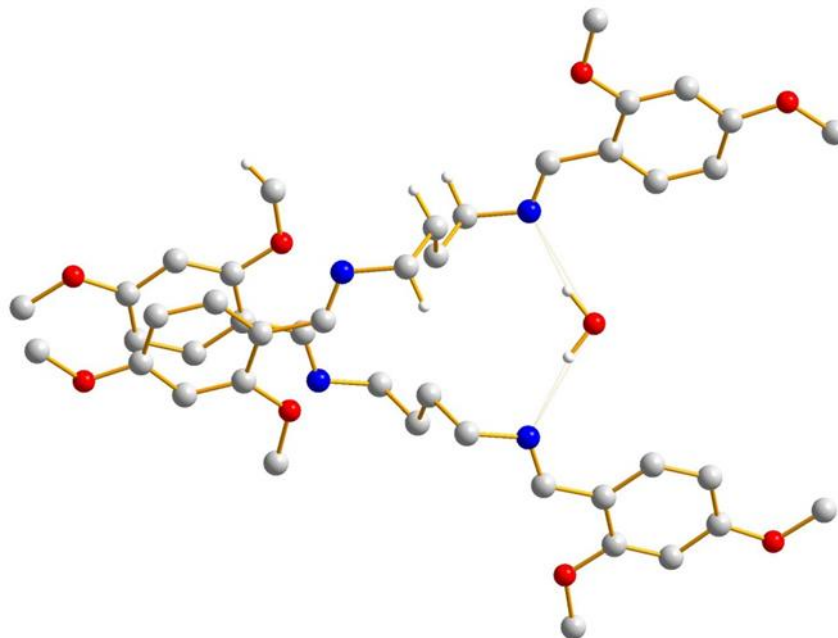


**Figure 2.** The represent planes for ligand

Hydrogen bonds between the water molecules of crystallization and iminic nitrogen atoms of (2,4-MeO-ba)<sub>2</sub>bn (Table 3) led to formation of a layered arrangement parallel to (100) (Figure 3).

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

D-H...A	D-H	H...A	D...A	D-H...A
O3W-H1W...N1 <sup>ii</sup>	0.95(2)	2.05(2)	2.9650(17)	163(2)

Symmetry codes: (ii)  $x, y, z-1$ **Figure 3.** The hydrogen bonds in the structure ligand. The hydrogen bonds shown as dashed lines

## Conclusions

In this work, Schiff-base compound *N,N'*-bis(2,4-dimethoxybenzylidene)-butane-1,4-diamine monohydrate ((2,4-MeO-ba)<sub>2</sub>bn/H<sub>2</sub>O) was prepared and characterized. The compound crystallized in the monoclinic space group *C2/c*. The N-C bond lengths of 1.2643 (19) and 1.457 (2) Å are typical of double and single bonds, respectively. Hydrogen bonds of the type O-H...N formed the layers propagating parallel to (100).

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