

## New 16-membered macrocyclic Schiff base: Synthesis, structural and FT-IR studies

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### Abstract

In this paper, the structure of a new 16-membered macrocyclic Schiff base compound N,N'-(3,3'-dimethoxy-2,2'-(propane-1,3-diylidioxo)dibenzylidene)propane-1,3-diamine, C<sub>22</sub>H<sub>26</sub>N<sub>2</sub>O<sub>4</sub> (1), derived from 1,3-propanediamine and 3,3'-dimethoxy-2,2'-(propane-1,3-diylidioxo)dibenzaldehyde has been studied by single crystal X-ray diffraction, DFT calculations at B3LYP/6-31G\*\* and FT-IR spectroscopy. The title compound was crystallized in the monoclinic space group *P*2<sub>1</sub>/*n* with unit cell parameters: *a* = 16.3273 (5) Å, *b* = 7.0832 (2) Å, *c* = 16.8586 (4) Å,  $\beta$  = 93.135 (2)°, *V* = 1946.77 (9) Å<sup>3</sup> and *Z*=4. The optimized molecular geometry agrees closely to that obtained from single crystal X-ray crystallography. The FT-IR spectrum (4000-400 cm<sup>-1</sup>) was recorded and compared with that of the calculated spectrum.

**Keywords:** Macrocyclic; Schiff base; single crystal; DFT calculations; monoclinic.

### Introduction

Macrocyclic Schiff base compounds have been widely studied for their importance in pharmacology [1-3] and for their potential applications in the fields of host-guest and supramolecular chemistry [4-7]. Methods for synthesis of macrocyclic Schiff base ligands are therefore very important. Many synthetic methods involve transition metal ions as templating agents [8-15]. By this way, stable macrocycle complexes which are generated complicate the preparation of metal-free macrocycle ligands. Therefore, many groups have been

concerned to develop metal free methods for the synthesis of macrocycle Schiff base compounds [16]. Recently, Reyes-Marquez and coworkers have reported the synthesis and structural characterization of macrocycle Schiff base compounds using a series of dialdehydes [17].

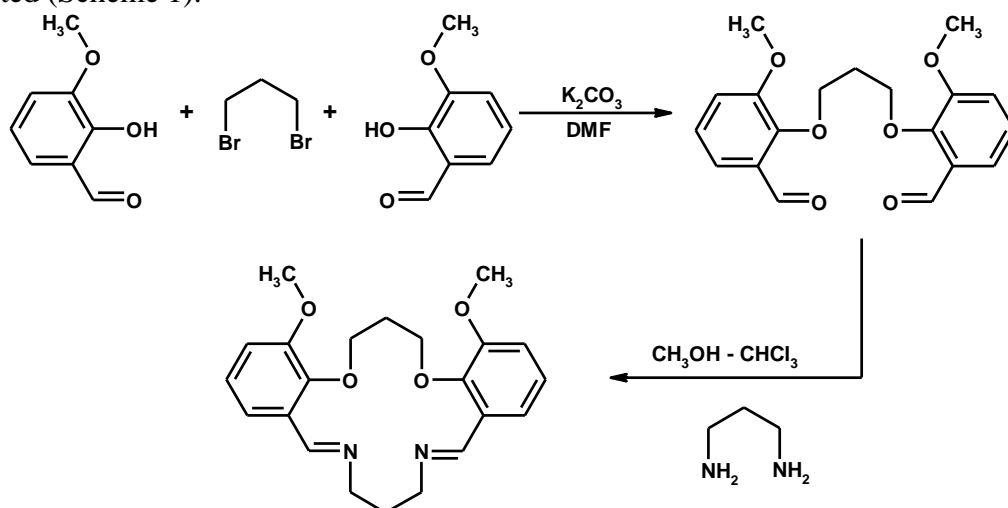
In the present work, the synthesis, structural characterization and FT-IR studies of a new 16-membered macrocyclic Schiff base compound N,N'-(3,3'-dimethoxy-2,2'-(propane-1,3-diylidioxo)dibenzylidene)propane-1,3-diamine, C<sub>22</sub>H<sub>26</sub>N<sub>2</sub>O<sub>4</sub> (1), derived from 1,3-propanediamine and 3,3'-

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dimethoxy-2,2'-(propane-1,3-diyldioxy)-dibenzaldehyde has been reported (Scheme 1).



**Scheme 1.** The chemical procedure of **1**

## Experimental

### Materials and physical measurements

All reagents and solvents for synthesis and analysis were commercially available and used as received without further purifications. Elemental analyses were carried out using a Heraeus CHN-O-Rapid analyzer. Infrared spectra were recorded using KBr disks on a FT-IR Perkin-Elmer spectrometer (Spectrum RX1). The 3,3'-dimethoxy-2,2'-(propane-1,3-diyldioxy)dibenzaldehyde used in this experiment was synthesized by condensation of 1,3-dibromopropane with 3-methoxysalicylaldehyde in *N,N*-dimethylformamide in the presence of anhydrous potassium carbonate according to the literature [18].

### Synthesis of **1**

3,3'-dimethoxy-2,2'-(propane-1,3-diyldioxy)-dibenzaldehyde (0.1 mmol) and 1,3-diaminopropane (0.1 mmol) were dissolved in a mixture of methanol-chloroform (1:1 v/v) at room temperature. The mixture was stirred at 50 °C for 1.5 h to give a clear solution. The mixture was cooled and allowed to

crystallize at room temperature. After keeping the solution in air for several 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. Yield: 75 %. *Anal. Calc.* for  $C_{22}H_{26}N_2O_4$ : C, 69.09 %; H, 6.85 %; N, 7.32 %. *Found*: C, 69.35 %; H, 6.71 %; N, 7.19 %. FT-IR ( $cm^{-1}$ ): 3010, 2923, 2888 (C-H aromatic and aliphatic), 2840 (-CH=N-), 1638 (-C=N-), 1579, 1475, 1453 (C=C).

### Computational details

The calculations were performed at DFT levels using the Gaussian 98 program [19]. The geometry of **1** was optimized by using the Hartree-Fock (HF) and density functional method (B3LYP) with a standard 6-311G\*\* basis set. The results, namely vibrational frequencies, geometry, bond length and bond angles were compared with the existing experimental data. The assignment of the experimental frequencies is based on the observed band frequencies and intensity changes in the infrared confirmed by

establishing one to one correlation between observed and theoretically calculated frequencies.

#### X-ray crystallography

A single crystal of the dimensions 0.26 mm × 0.16 mm × 0.14 mm of **1** was chosen for the X-ray diffraction study. Crystallographic measurements were done at 120 K with four circle CCD diffractometer Gemini of Oxford diffraction, Ltd., with mirrors-collimated Cu  $K\alpha$  radiation ( $\lambda = 1.54184 \text{ \AA}$ ). The crystal structure was solved by charge flipping with the program SUPERFLIP [20] and refined with the Jana2006 program package [21] by full-matrix least-squares technique on  $F^2$ . The molecular structure plots were prepared by

ORTEP III [22]. Hydrogen atoms were mostly discernible in difference Fourier maps and could be refined to a reasonable geometry. Crystallographic data and details of the data collection and structure solution and refinements are listed in Table 1.

The unit cell angles were close to orthorhombic ones. Due to this geometric predisposition a pseudomeroherdic twinning occurred as a  $180^\circ$  rotation around the reciprocal axis  $a^*$ . The refined volume fraction of the minor twin component was 0.2180(6). Introducing of twinning was important for successful refinement of the crystal structure.

**Table 1.** Crystal data and structure refinement parameters of **1**

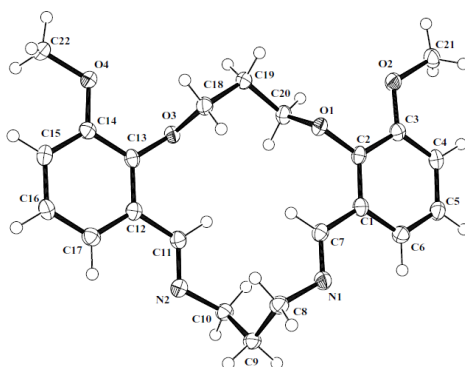
Empirical formula	$C_{22}H_{26}N_2O_4$
Formula weight	382.45
Crystal system	Monoclinic
Space group	$P2_1/n$
$a$ (Å)	16.3273 (5)
$b$ (Å)	7.0832 (2)
$c$ (Å)	16.8586 (4)
$\beta$ (degree)	93.135 (2)
$V$ (Å <sup>3</sup> )	1946.77 (9)
$Z$	4
$\mu$ (mm <sup>-1</sup> )	0.73
Measured reflections	6674
Independent reflections	6641
Parameters	254
Reflection with $I > 3\sigma(I)$	4599
$R_{\text{int}}, S$	0.032, 1.19
$R[F^2 > 2\sigma(F^2)], wR(F^2)$	0.038, 0.096
$\Delta\rho_{\text{max}}$ (eÅ <sup>-3</sup> ), $\Delta\rho_{\text{min}}$ (eÅ <sup>-3</sup> )	0.18, -0.13
$T_{\text{min}}, T_{\text{max}}$	0.004, 1

### Molecular geometry

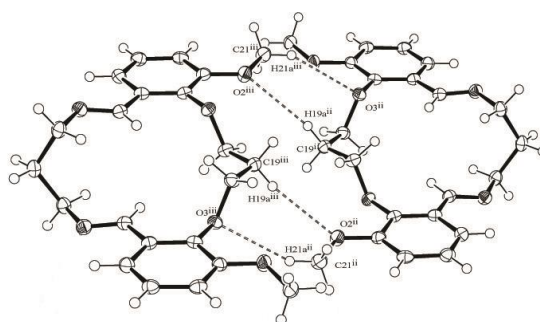
The molecular structure of the title compound **1** with the atom-numbering scheme is shown in Figure 1, and the selected bond distances and angles are given in Table 2. As could be seen, the molecular structure was not planar. The X-ray single crystal structure determination indicates that the cell structure of **1** contains four independent structural units belonging to monoclinic system with space group of  $P2_1/n$ .

As seen at Table 2, the experimental and theoretical bond distances and angles slightly differ, and in the theoretical calculation the compound **1** has been considered in the gaseous phase that differs from the solid state [24]. The N1-C7 (1.2686(14)), N2-C11 (1.2725(14)), N1-C8 (1.4541(16)) and N2-C10

(1.4565(15) Å) bond distances are consistent with the distances of the C-N double and single bonds as presented for the related compounds previously studied [17,23]. The bond angles C7-N1-C8 (117.94(10)) and C10-N2-C11 (117.70(10)) are consistent with the  $sp^2$  hybrid character of N1 and N2 atoms and are similar to other macrocycle reported Schiff bases [17,23]. The distance between the two nitrogen atoms N1 and N2 is 3.879 Å, while the distance between the two nitrogen atoms O1 and O3 is 3.956 Å and are shorter than the distances between the oxygen and nitrogen atoms (4.086 and 5.652 Å). In **1**, there are two inter-molecular hydrogen bonds (Figure 2, Table 3).



**Figure 1.** The molecular structure of **1**; Thermal ellipsoids have been drawn at the 50% probability level.



**Figure 2.** Part of the crystal structure of **1** showing the inter-molecular hydrogen bonds as dashed lines

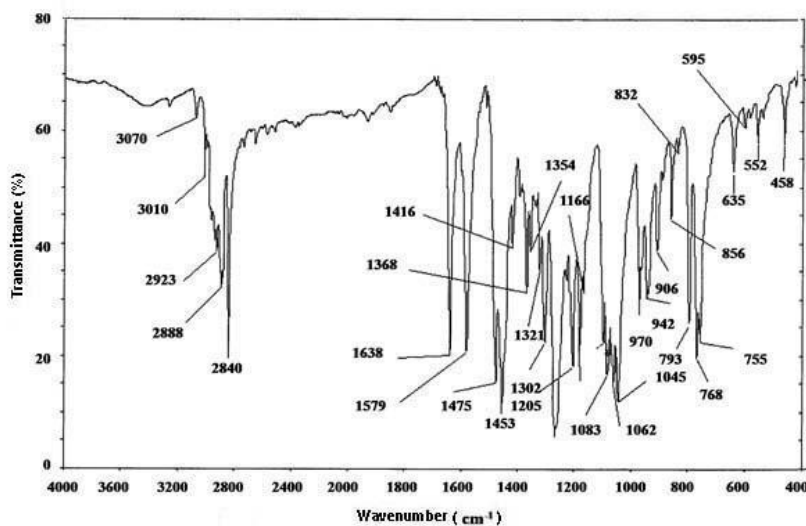
### Theoretical studies

Theoretical study was carried out to evaluate the spatial orientation of the compound. We explored that there is one optimized structure of **1** that was supported by the X-ray structure. The selected bond distances and angles for the optimized structure are listed in Table 2. The detailed assignments for the selected vibrational spectra are given in Table 4.

The Fourier transform infrared (FT-IR) spectrum of the title compound **1** is depicted in Figure 3. The aromatic and aliphatic C-H vibrations are observed between 3050-2845  $\text{cm}^{-1}$ . The theoretical C-H aromatic and aliphatic vibrations are assigned in the region 3150–2981  $\text{cm}^{-1}$  (B3LYP), which are in good agreement with the structural data.

In the title compound **1**, there are several C-C vibrations. The aromatic C=C stretching vibrations appear in the range 1723-1471  $\text{cm}^{-1}$ , which are in good agreement with theoretically calculated data. In the FTIR spectrum of **1**, the ring breathing mode appears as a weak band at 1204 and 1180  $\text{cm}^{-1}$ , while bands appearing at 755 and 767  $\text{cm}^{-1}$  are assigned to the deformation of phenyl ring, which are in good agreement with theoretically calculated data between 1261-1233  $\text{cm}^{-1}$ , 1131-1119 and 796-733  $\text{cm}^{-1}$ .

The C=N stretching of **1** appears in the region 1637  $\text{cm}^{-1}$ , while the C-N stretching vibrations appear at 1044-1096  $\text{cm}^{-1}$ . We observed the C=N stretching vibration mode at 1633  $\text{cm}^{-1}$  and the C-N stretching vibrations at 1021 and 962  $\text{cm}^{-1}$ .



**Figure 3.** The FT-IR spectrum of **1**

From the theoretical calculations, it is observed that the C-H out-of-plane vibration modes display very weak bands at below 1000  $\text{cm}^{-1}$ . According to the theoretical calculations, the corresponding bands appear at 970  $\text{cm}^{-1}$  (C-H aromatic), 942  $\text{cm}^{-1}$  (N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-N), and 906  $\text{cm}^{-1}$  (O-CH<sub>2</sub>) (Table 4) [23-25]. The bands observed at about 458, 552, 595 and 635  $\text{cm}^{-1}$  are ascribed

to the phenyl ring angle bending modes [24].

The calculated HOMO–LUMO plots of **1** using B3LYP with 6-311G\*\* level basis set are shown in Figure 3. As seen in Figure 4, the HOMO orbital is localized on the aromatic rings as well as the oxygen atoms and methoxy groups, while the LUMO is localized on the aromatic rings as well as the azomethine (C=N) groups. The value of

the energy separation between the HOMO (5.834 eV) and LUMO (0.962 eV) is 4.872 eV, and this large energy

gap indicates that the title compound is very stable.

**Table 2.** Selected bond distances and angles of 1<sup>a</sup>

	Experimental	Theoretical		Experimental	Theoretical
N1-C7	1.2686(14)	1.276	N1-C8	1.4541(16)	1.455
N2-C11	1.2725(14)	1.276	N2-C10	1.4565(15)	1.455
C1-C7	1.4740(17)	1.475	C11-C12	1.4708(16)	1.475
O1-C2	1.3856(14)	1.375	O1-C20	1.4447(14)	1.444
O3-C13	1.3849(14)	1.375	O3-C18	1.4466(15)	1.444
C18-C19	1.5168(17)	1.522	C19-C20	1.5153(16)	1.521
C10-C9	1.5259(16)	1.537	C9-C8	1.5237(17)	1.537
O4-C14	1.390(13)	1.368	O4-C22	1.4332(15)	1.419
O2-C3	1.3652(13)	1.368	O2-C21	1.4337(15)	1.419
C1-C7- N1	121.26(11)	121.90	C7-N1-C8	117.94(10)	118.09
N1-C8- C9	109.87(10)	110.95	C8-C9- C10	112.77(9)	113.87
C9-C10- N2	109.67(10)	110.95	C10-N2- C11	117.70(10)	118.09
N2-C11- C12	121.57(11)	121.89	C11-C12- C13	120.05(10)	119.96
C12-C13- O3	119.70(10)	119.85	C13-O3- C18	113.12(9)	116.23
O3-C18- C19	108.23(9)	107.76	C18-C19- C20	115.25(9)	115.05
C19-C20- O1	108.18(9)	107.76	C20-O1- C2	112.97(8)	116.24
O1-C2- C1	119.90(10)	119.84	C2-C1-C7	119.96(10)	119.96
C22-O4- C14	116.56(9)	118.08	O4-C14- C13	115.97(10)	115.71
C21-O2- C3	116.88(9)	118.08	O2-C3-C2	115.78(10)	115.71
O4-C14- C15	124.18(10)	124.57	O2-C3-C4	124.47(11)	124.57

a) Calculated at the B3LYP/6-311G\*\* level; the figures in brackets provide the uncertainty in the last decimal figures.

**Table 3.** Hydrogen bonds parameters (Å, °) for **1**

Hydrogen bonding	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A (°)
C19-H19a···O2	0.960	2.732	3.667	164.745
C21-H21a···O3	0.960	2.792	3.610	143.556

**Table 4.** The calculated vibrational frequencies (cm<sup>-1</sup>) and approximate assignment for **1**

Theor.	Exp.	Vibrational assignments
3080	3070 (w)	va (CH <sub>3</sub> )
3038	3010 (w)	vs (CH <sub>2</sub> )
3017	2973 (w)	vs (CH <sub>3</sub> )
3017	2945 (w)	vs (CH <sub>3</sub> )
2983	2922 (s)	vs (CH <sub>2</sub> )
2981	2888 (vs)	vs (CH <sub>2</sub> )
1633	1637 (vs)	8b, v (C=N)
1529	1578 (vs)	δ (CH <sub>2</sub> )
1476	1475 (s)	(CH <sub>2</sub> ) sci
1471	1453 (s)	(CH <sub>2</sub> ) sci
1413	1416 (w)	ρ (CH <sub>2</sub> ), δ (CH)
1364	1368 (s)	δ (CH <sub>2</sub> ), δ (CH), ω (CH <sub>2</sub> ), ω (CH <sub>3</sub> )
1354	1354 (w)	14, δ (CH <sub>2</sub> ), ρ (CH <sub>3</sub> ), δ (CH)
1325	1320 (s)	τ (CH <sub>2</sub> )
1305	1302 (s)	v (CH <sub>3</sub> -O-ph), δ (CH <sub>3</sub> ,14), ω (CH <sub>2</sub> )
1261	1267 (vs)	τ (CH <sub>2</sub> ), δ (CH <sub>3</sub> )
1212	1205 (s)	9a, δa (CH <sub>3</sub> ), v (O-ph), δ (CH)
1178	1180 (s)	τ (CH <sub>3</sub> )
1178	1167 (vw)	τ (CH <sub>3</sub> )
1100	1096 (vw)	v (O-CH <sub>3</sub> ), ρ (CH <sub>2</sub> ), ω (CH <sub>2</sub> )
1080	1082 (w)	v (O – CH <sub>3</sub> ), δ (CH <sub>2</sub> )
1071	1061 (w)	δ (CH <sub>2</sub> )
1032	1044 (s)	v(O –CH <sub>3</sub> ), δ (CH), τ (CH <sub>2</sub> )
973	970 (s)	17b, v (O – CH <sub>3</sub> ), δ (CH <sub>2</sub> )
950	942 (s)	δ (N=C-H), ρ(CH <sub>2</sub> ), v(CH <sub>3</sub> -O-ph), ω(CH <sub>2</sub> )
905	905 (s)	v (C-C-C), δ (CH <sub>2</sub> ), ω (CH)



866	855 (s)	$\omega$ (CH <sub>3</sub> ), $\omega$ (CH <sub>2</sub> ), $\rho$ (CH <sub>2</sub> )
838	831 (w)	6b, $\tau$ (CH <sub>2</sub> ), $\rho$ (CH <sub>2</sub> )
796	793 (vs)	11, $\omega$ (CH <sub>3</sub> ), $\omega$ (CH <sub>2</sub> ), $\omega$ (CH)
775	767 (vs)	$\delta$ (CH), $\omega$ (CH <sub>3</sub> ), $\omega$ (CH <sub>2</sub> ), $\omega$ (CH)
758	755 (vs)	$\delta$ (CH), $\rho$ (CH <sub>2</sub> ), $\omega$ (CH)

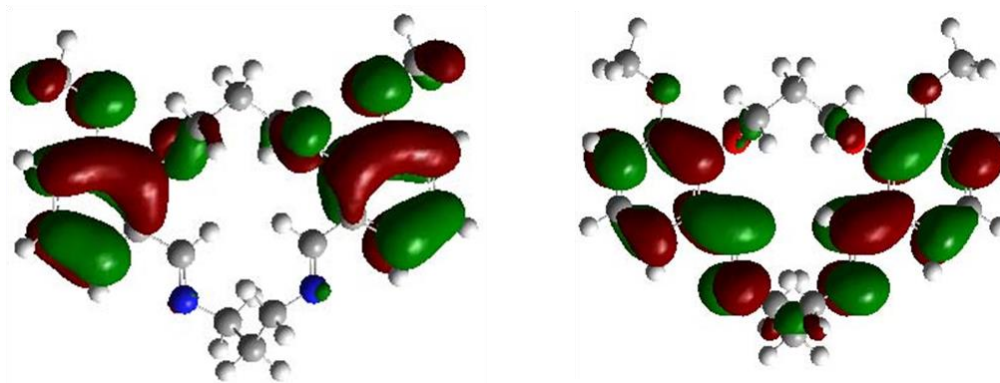
$\tilde{\nu}_F$ : Theoretical frequency calculated at B3LYP/6-31G\*\* level; I<sub>IR</sub>, IR intensity (km/mol),

v: stretching,  $\gamma$ : out-of-plane bending,  $\delta$ : in-plane bending,  $\tau$ : torsion,  $\Gamma$ : out-of-plane ring deformation,  $\omega$ : wagging,  $\Delta$ : In plane ring deformation [23]

### Conclusion

A new 16-membered macrocyclic Schiff base compound N,N'-(3,3'-dimethoxy-2,2'-(propane-1,3-diylidioxy)dibenzylidene)-propane-1,3-diamine has been synthesized and characterized by elemental analysis, FT-IR spectroscopy and single crystal X-ray diffraction. The quantum

chemical method (at B3LYP/6-31G\*\* level) was used to obtain geometrical parameters and to calculate the FT-IR spectrum of the compound, which is compared with the experimental one. The geometrical bond distances and angles are in agreement with the results from X-ray crystallography.



**Figure 4.** Frontier molecular orbitals of 1

### Acknowledgements

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### Supplementary Data

Crystallographic data (excluding structure factors) for the structure

reported in this paper has been deposited with the Cambridge Crystallographic Center, CCDC No. 998578. Copies of the data can be obtained free of charge on <http://www.ccdc.cam.ac.uk>.

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