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ORIGINAL PAPER

Synthesis, Characterization and Crystal Structure of *N*,*N*′-Bis(2,3-Dimethoxybenzylidene)-1,2-Diaminoethane

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Abstract Synthesis and characterization of single crystals of a new organic Schiff-base derivative, *N*,*N*′-bis(2,3-dimethoxybenzylidene)-1,2-diaminoethane is reported. Good quality single crystals with size 10 mm × 1 mm × 1 mm were grown by slow evaporation technique from a methanol solution at room temperature. The grown crystals have been characterized by elemental analyses and functional groups were identified using FT-IR and ^{1}H-NMR spectroscopy. Crystal structure of the title compound has been determined by single crystal X-ray diffraction. The title compound has a monoclinic symmetry, space group $P2_1/c$, lattice parameters are $a = 4.4159(3)$ Å, $b = 14.2333(9)$ Å, $c = 15.0601(10)$ Å, $\beta = 97.755(5)°$, $Z = 2$, $V = 937.91(11)$ Å^3.

Keywords Characterization · Single crystals · Schiff-base · X-ray diffraction

Introduction

Schiff base compounds, having imine groups (–CH=N–), are widely studied during recent years due to their different applications in various areas, such as nonlinear optic [1], photochromism [2], antimicrobial activity [3] and anion sensor [4]. Schiff-bases compounds, an important class of organic materials, which shown good crystallizability, have been extensively studied as a corrosion inhibitors for steel and iron [5, 6]. These compounds are typically formed by the condensation of suitable amines and aldehydes [7–10]. They have been extensively studied as ligands in the development of coordination compounds of transition metals [11–15]. On the industrial scale, they have wide range of applications such as dyes and pigments [16].

As an additional contribution to the synthesis, characterization and crystal structures of Schiff-base compounds and theirs transition metal complexes and in the course of our ongoing studies of these kinds of materials [17–30] in this work, we report the synthesis of bidentate Schiff-base ligand *N*,*N*′-bis-(2,3-dimethoxybenzylidene)-1,2-diaminoethane (Scheme 1) and growth of its crystals from methanol solution. The grown crystals were characterized by crystal structure determination by single crystal X-ray diffraction, FT-IR, ^{1}H-NMR and elemental analyses.

Experimental Procedure

Physical Techniques and Materials

All reagents (2,3-methoxybenzaldehyde and ethylenediamine) and solvent (methanol) for synthesis, growth and analysis were commercially available and used as received without further purification. Elemental analyses were carried out using a Heraeus CHN-O-Rapid analyzer. ^{1}H-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

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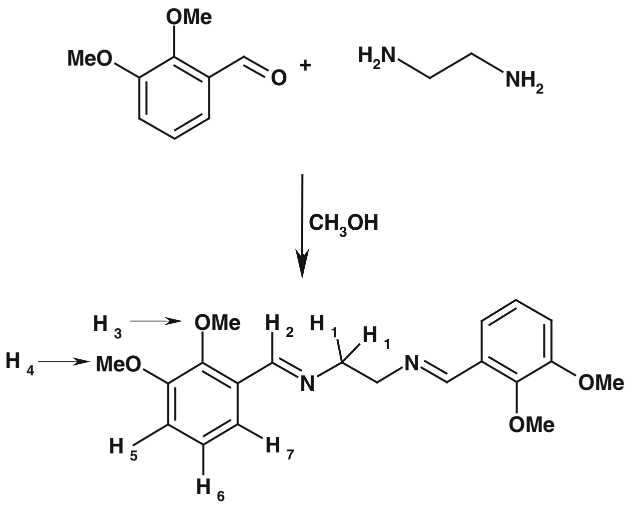

Scheme 1 Structure of ligands *N*,*N*′-bis-(2,3-dimethoxybenzylidene)-1,2-diaminoethane

spectrum was recorded on a JASCO 680 plus FT-IR spectrophotometer as a KBr pellet.

Preparation and Crystal Growth

A solution of 2,3-dimethoxybenzaldehyde (3.30 g, 0.02 mol) in 25 ml methanol was heated for 15 min at 50 °C and then stirred for about 15 min. To this stirring solution, a solution of ethylenediamine (0.6 g, 0.01 mol) in 15 ml methanol was added dropwise with constant stirring. The mixture was heated at about 50 °C for 1.5 h and then allowed to cool for overnight at 273 K. The resulting crude solid was collected by filtration and dried at room temperature. Crystals were grown by the slow evaporation technique at room temperature in 25 ml methanol as a solvent for 5 days. At the period of super saturation, tiny crystals were nucleated. They were allowed to grow to a maximum possible dimension and then filtered. Yield: 3.03 g, 85%. Colorless crystals. *Anal*. Calc. for $C_{20}H_{24}N_2O_4$: C, 67.42; H, 6.74; N, 7.86%. Found: C, 67.35; H, 6.69; N, 7.79%. IR (KBr pellet, cm^{-1}): 2830–3010 (m, C–H aromatic and aliphatic), 1639 (s, C=N). ^{1}H-NMR ($CDCl_3$, δ(ppm)): 3.76 (s, 6$\mathbf{H_3}$), 3.84 (s, 6$\mathbf{H_4}$), 3.99 (s, 4$\mathbf{H_1}$), 6.91 (dd, 2$\mathbf{H_7}$), 7.02 (t, 2$\mathbf{H_6}$), 7.51 (dd, 2$\mathbf{H_5}$), 8.64 (s, 2$\mathbf{H_2}$).

The solubility of the title compound was determined by adding the solvent to a known amount of compound until completely dissolved. It was found that the synthesized compound is moderately soluble in methanol (0.15 g/ml), ethanol (<0.15 g/ml) and acetonitrile (0.17 g/ml), insoluble in water and completely soluble in chloroform ($\approx$70 g/ml) and dichloromethane ($\approx$70 g/ml). However, this compound is moderately soluble in ethanol and acetonitrile, we can't get suitable crystals from these solvents. The resulting grown colorless transparent crystals of maximum dimension 10 mm × 1 mm × 1 mm are shown in Fig. 1.

Characterization

Synthesis and Characterization

Reaction between 2,3-dimethoxybenzaldehyde and ethylenediamine at suitable temperature yielded the bidentate Schiff-base ligand *N*,*N*′-bis-(2,3-dimethoxybenzylidene)-1,2-diaminoethane (see Scheme 1). The title compound is air-stable in the solid state for about 3–5 months. It is very slightly soluble in common organic solvents such as acetonitrile and methanol but completely soluble in chloroform and dichloromethane. The stability of dissolved compound is much shorter than in the solid state and depends on the nature of the solvent. In methanol and

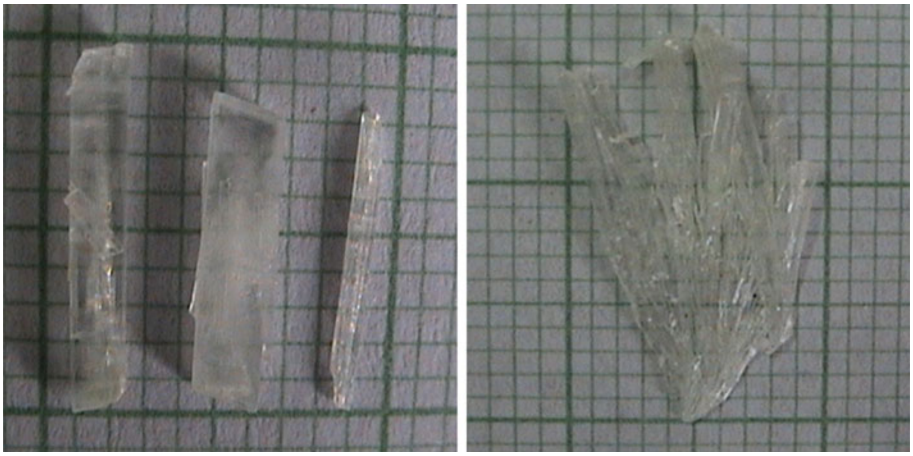

Fig. 1 Single crystals of *N*,*N*′-bis-(2,3-dimethoxybenzylidene)-1,2-diaminoethane

acetonitrile solution it is stable about 10 days at room temperature and about 30 days at 273 K. In chloroform and dichloromethane it remains unchanged for about 1 day at room temperature and about 3 days at 273 K.

In order to confirm the chemical composition of the synthesized compound, CHN analysis was carried out on the recrystallized sample. The result of the analysis is presented in the experimental section. Theoretical values of CHN have suggested the molecular formula $C_{20}H_{24}N_2O_4$. The experimental and calculated values of C, H, and N agree with each other, confirming the formation of $C_{20}H_{24}N_2O_4$.

The ^{1}H-NMR spectra of *N*,*N*′-bis-(2,3-dimethoxybenzylidene)-1,2-diaminoethane (Fig. 2) display two singlet signals at 3.75 and 3.83 ppm which are assigned to protons of the methoxy groups, H_3 and H_4, respectively, and one singlet signal at 3.99 ppm assigned to protons of H_1. One triplet signal at 7.02 ppm is assigned to aromatic H_6 protons, while two doublets of doublet signals at 6.91 and 7.51 ppm are assigned to aromatic H_7 and H_5 protons, respectively. One singlet signal at 8.64 ppm is assigned to C=N group (H_2).

The FT-IR analysis of *N*,*N*′-bis-(2,3-dimethoxybenzylidene)-1,2-diaminoethane was carried out to investigate the presence of functional groups and their vibrational modes. The spectrum was recorded between 400 and 4,000 cm^{-1} using a JASCO 680 plus FT-IR spectrophotometer. The relatively weak absorption bands around 2,830–3,010 cm^{-1} was assigned to the C–H vibration modes involving the aromatic and aliphatic hydrogen atoms and variable intensity around 1,400–1,600 cm^{-1} correspond to vibrations of the aromatic rings of the title compound, while the strong and sharp stretching vibration at 1,639 cm^{-1} was assigned to *ν*(C=N).

Single Crystal X-ray Analysis

A single crystal of the title compound with the dimensions 0.42 mm × 0.07 mm × 0.07 mm was chosen for X-ray diffraction study. Crystallographic measurements were done at room temperature with four circle CCD diffractometer Geminy of Oxford diffraction, Ltd., mirrors-collimated Cu *Kα* radiation ($\lambda = 0.54184$ Å). The crystal structures were solved by direct methods with program SIR2002 [31] and refined with program package Jana2006 [32] by full-matrix least-squares technique on F^2. The molecular structure plots were prepared by ORTEP III [33]. 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 $1.2U_{\mathrm{eq}}$ of the parent atom. Crystallographic data and details of the data collection and structure refinements are listed in Table 1. Selected bond distances and angles are listed in Table 2.

The ORTEP diagram (Fig. 3) shows the title compound *N*,*N*′-bis-(2,3-dimethoxybenzylidene)-1,2-diaminoethane with

Fig. 2 ^{1}H-NMR spectra of *N*,*N*′-bis-(2,3-dimethoxybenzylidene)-1,2-diaminoethane

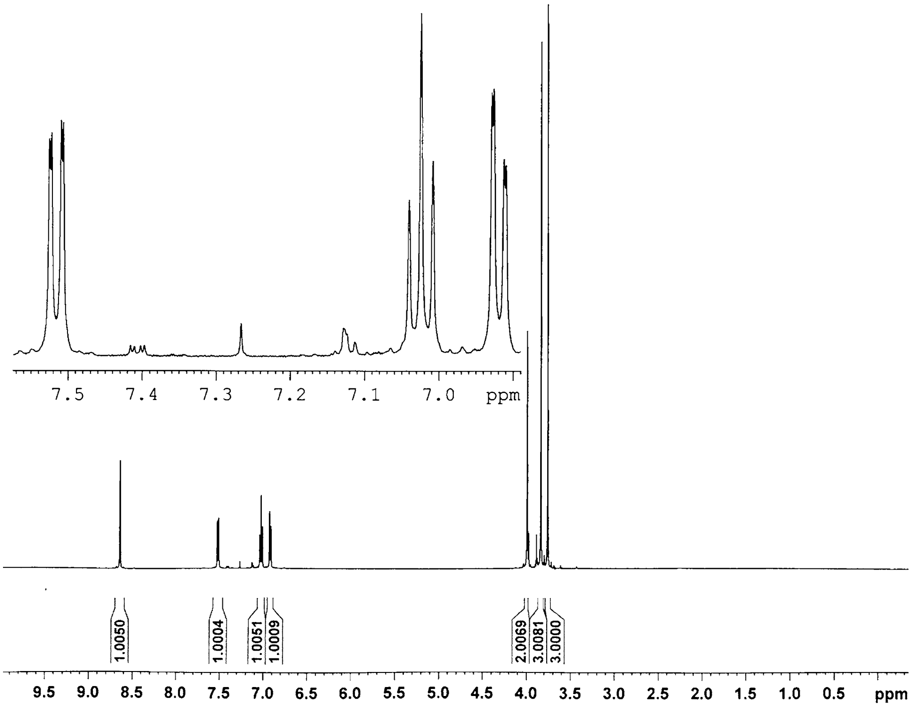

Table 1 Crystallographic and structure refinement of the title compound

Empirical formula	$C_{20}H_{24}N_2O_4$
Formula weight	356.4
Wavelength (Å)	1.5418
Crystal system, Space group	Monoclinic, $P2_1/c$
T (K)	295
a (Å)	4.4159(3)
b (Å)	14.2333(9)
c (Å)	15.0601(10)
β (deg)	97.755(5)
V (Å^3)	937.91(11)
Z	2
μ (mm^{-1})	0.72
Density Mg m^{-3}	1.261
$T_{\min}$	0.708
$T_{\max}$	0.949
F_{000}	380
Measured reflections	3987
Independent reflections	1441
Reflection with $I > 3\sigma(I)$	1157
R_{int}	0.014
S	1.98
$R[F^2 > 2\sigma(F^2)]$	0.037
$wR(F^2)$	0.111
Parameters	118
$\Delta\rho_{\max}$ (e Å^{-3})	0.12
$\Delta\rho_{\min}$ (e Å^{-3})	−0.12
Crystal size (mm^3)	0.42 × 0.07 × 0.07
Index ranges	$-4 \le h \le 2$; $-16 \le k \le 16$; $-14 \le l \le 17$

Table 2 Selected bond lengths (Å) and angles (°) of the title compound

O1–C2	1.3791(17)	O2–C10	1.421(2)
O1–C9	1.429(2)	N1–C7	1.251(2)
O2–C3	1.357(2)	N1–C8	1.456(2)
N1–C8–C8^i	111.34(13)	N1–C7–C1	123.24(14)
C7–N1–C8	117.84(14)	C2–O1–C9	115.19(12)
C3–O2–C10	117.69(13)	O2–C3–C2	115.99(13)
O1–C2–C1	119.31(13)	O2–C3–C4	125.12(15)
O1–C2–C3	119.72(14)		

Symmetry codes: (i) −x + 1, −y, −z + 1

the displacement ellipsoids of all non-hydrogen atoms at 40% probability level. Selected bond distances and angles (Table 2) are in good agreement with those reported in similar Schiff-base compounds [17–19, 29]. The symmetry equivalent C=N double bonds C7–N1 and C7^i–N1^i (Fig. 3a). The C7=N1 bond length of 1.251 (2) Å conforms to the value for a double bond while the bond length of C8–N1, 1.456 (2) Å, conforms to the value for a single bond. Similar situation can be found in (*E*,*E*)-*N*,*N′*-bis-(3,4,5-dimethoxybenzylidene)ethylenediamine [18], where the bond lengths of C2=N1and C1–N1 are 1.257 (3) and 1.643 (2) Å, respectively. The bond angles C1–C7–N1 and C7–N1–C8 are 123.24(14) and 117.84(14), respectively, and they are consistent with the sp^2 hybrid character for C7 and N1 atoms [17–19, 29]. The torsion angles of the title compound, C2–C1–C7–N1, C1–C7–N1–C8 and C7–N1–C8–C8^i are −167.188(149)°, −177.791(139)° and −126.326 (158)°, respectively, indicating a virtually planar *E*-configuration with respect to the imine C=N bond. There are intermolecular O···H–C hydrogen bonds in the crystal packing of the title compound *N*,*N′*-bis-(2,3-dimethoxybenzylidene)-1,2-diaminoethane that shown in Fig. 4. The investigated samples exhibited single crystal diffraction down to 170 K. Below this temperature they were damaged and only very weak powder-like diffraction could be observed. This occurred regularly for slow as well as fast cooling with all of the ten tested samples. The structure at 170 K was calculated and compared with the one measured at room temperature. Both structures were identical except small rotation of methyl groups. Probably a destructive phase transition occurs below 170 K which cannot be investigated by means of single-crystal X-ray diffraction due to cracking of the samples.

Conclusions

The new bidentate Schiff-base derivative, *N*,*N′*-bis-(2,3-dimethoxybenzylidene)-1,2-diaminoethane, was synthesized and characterized by elemental analyses, FT-IR and ^{1}H-NMR spectroscopy. Single crystals were successfully grown from solution by slow evaporation technique at room temperature using a 25 ml methanol as a solvent. FT-IR and ^{1}H-NMR are used to confirm the functional groups, particularly –HC=N imine group. The single crystal X-ray diffraction has revealed a monoclinic structure with space group $P2_1$/c, lattice parameters $a = 4.4159(3)$ Å, $b = 14.2333(9)$ Å, $c = 15.0601(10)$ Å, $\beta = 97.755(5)°$ and one symmetry independent molecule $C_{20}H_{24}N_2O_4$ in almost planar *E*-configuration with respect to the imine C=N bond.

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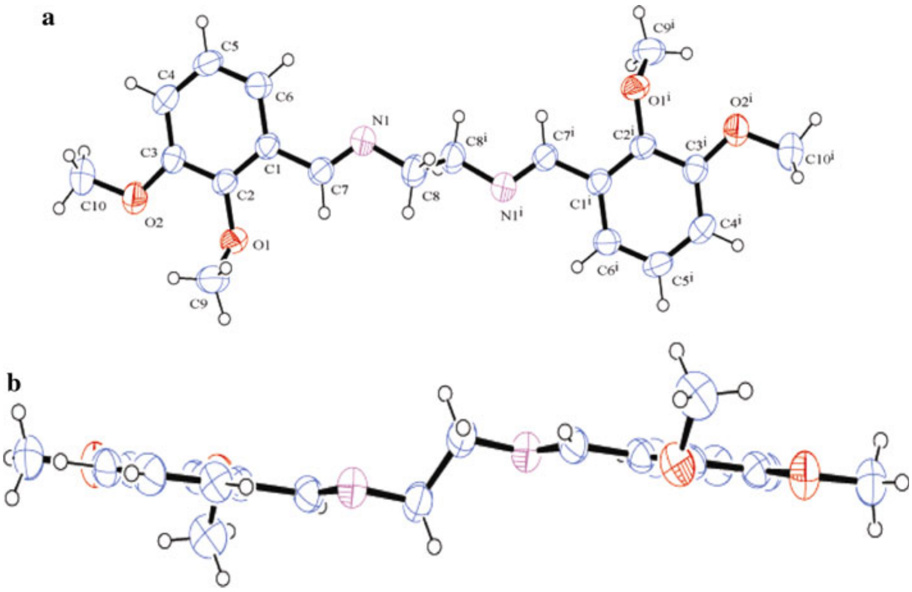

Fig. 3 ORTEP view of *N*,*N*′-bis-(2,3-dimethoxybenzylidene)-1,2-diaminoethane, showing 40% probability displacement ellipsoids and the atomic numbering (**a**), non-planar and centre of symmetry (**b**)

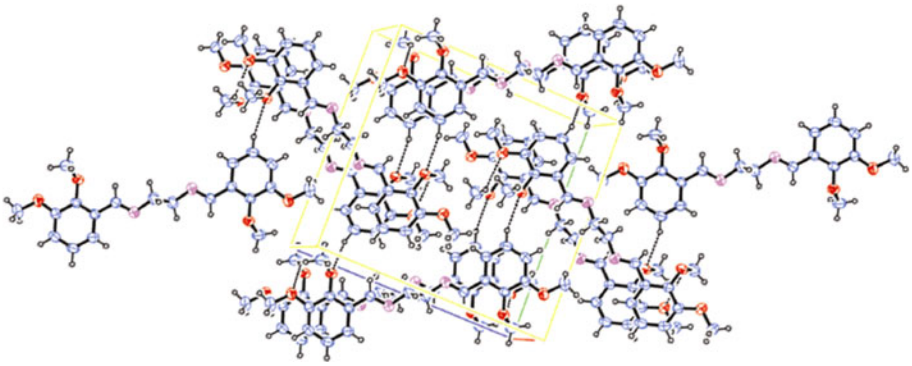

Fig. 4 Packing diagram of *N*,*N*′-bis-(2,3-dimethoxybenzylidene)-1,2-diaminoethane along *a* axis. *Dashed lines* represent hydrogen bonds

Appendix A. Supplementary Data

Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Center, CCDC Nos. 731883. 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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