

Synthesis and crystal structure of Schiff-base compound (E)-4-methoxy-N-(4-hydroxybenzylidene) aniline

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Abstract: New Schiff-base compound (E)-4-methoxy-N-(4-hydroxybenzylidene) aniline has been synthesized from the reaction of 4-hydroxybenzaldehyde with 4-methoxyaniline in methanol at 50°C, and has been characterized by using elemental analysis and FT-IR spectroscopy. The crystal structure of the title compound has been determined by single crystal X-ray diffraction study. The title compound crystallizes in the orthorhombic, space group Pbcn with unit cell parameters $a = 22.3813(5)$, $b = 10.7477(2)$, $c = 9.3623(2)$ Å, $V = 2252.08(8)$ Å³, $Z = 8$ and $R = 0.03$. The N1 = C7 imine bond length of 1.2839(14) Å is typical of a double bond. The molecule of the title compound is non planar and the dihedral angle between the two phenyl rings is 58.97 (32)°. There is a strong intermolecular hydrogen bond of the O···H-C type forming one-dimensional chain.

Keywords: Schiff-base; crystal structure; one-dimensional chain.

Introduction

Interest in Schiff-base compounds has increased greatly during recent years due to their different structures (symmetry and asymmetry) [1-4] and properties such as anion sensitivity [5], photochromism and thermochromism [6], nonlinear optics [7,8] and antimicrobial activity [9,10]. They have been widely used as ligands in the formation of transition metal complexes [9]. As a continuation of our previous work [11-13], the structure of new Schiff-base compound (E)-4-methoxy-N-(4-hydroxybenzylidene) aniline is reported here.

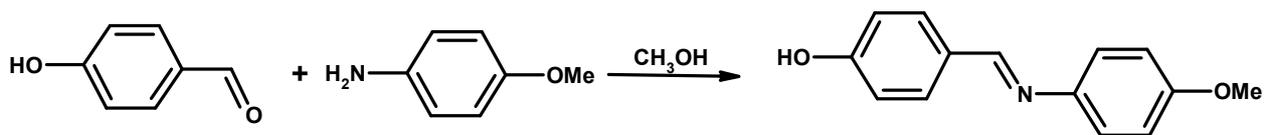
Experimental

All reagents and solvents for synthesis and analysis were commercially available and used as received. 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.

Synthesis of (E)-4-methoxy-N-(4-hydroxybenzylidene) aniline (1)

A solution of 4-hydroxybenzaldehyde (1.22 g, 0.01 mol) in 25 ml methanol was heated for 10 min at 50°C and then stirred for about 25 min. To this stirring solution, a solution of 4-methoxyaniline (1.23 g, 0.01 mol) in 20 ml methanol was added dropwise under constant stirring. The mixture was heated at about 50°C for 2 h and then allowed to cool overnight to room temperature. The resulting crude solid was collected by filtration and dried at room temperature (Scheme 1). Yellow crystals were grown by the slow evaporation technique at room temperature in a mixture of methanol and chloroform (25 ml, 1.5:1 v/v) as a solvent for 2 days. Yield: 1.99 g, 88%. Anal. Calc. for C₁₄H₁₃NO₂: C, 73.99; H, 5.77; N, 6.16%. Found: C, 74.04; H, 5.67; N, 6.24 %. IR (KBr pellet, cm⁻¹): 2838 (O-H···N hydrogen bond), 2863-2971 (C-H aliphatic), 3004-3067 (C-H, aromatic), 1605 (s, C = N), 1442-1577 (C = C aromatic).

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Scheme 1

X-ray crystallography

Crystallographic measurements were done at 120 K with four circle CCD diffractometer Gemini of Oxford diffraction, Ltd., with mirrors-collimated Cu K α radiation ($\lambda = 1.54184 \text{ \AA}$). The crystal structure was solved by direct methods with program SIR2002 [14] and refined with the Jana 2006 program package [15] by full-matrix least-squares technique on F^2 . The molecular structure plots were prepared by ORTEP III [16]. 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 $1.2U_{eq}$ of the parent atom. Crystallographic data

and details of the data collection and structure refinements are listed in Table 1. The final atomic coordinates and thermal parameters for non-hydrogen atoms are listed in Table 2.

Results and Discussion

Synthesis

The title compound 1 was obtained in high yield, 88%, by mixing equimolar amounts of 4-hydroxybenzaldehyde and 4-methoxyaniline. The title compound is stable in the solid state, while the stability of dissolved compound is much shorter than in the solid state and depends on the nature of the solvent [11,12]. The title compound is very slightly soluble in common organic solvents such as acetonitrile and methanol but completely soluble in chloroform and dichloromethane.

Table 1 Crystal Data for 1.

Empirical formula	C ₁₄ H ₁₃ NO ₂
Formula weight	227.3
Crystal system, Space group	Orthorhombic, Pbcn
T (K)	120
a (Å)	22.3813(5)
b (Å)	10.7477(2)
c (Å)	9.3623(2)
V (Å ³)	2252.08(8)
Z	8
μ (mm ⁻¹)	0.73
T _{min} , T _{max}	0.753, 1.000
Measured reflections	24264
Independent reflections	1957
Reflection with $I \geq 3\sigma(I)$	1676
R _{int}	0.033
S	1.82
R[F ² > 3 σ (F ²)]	0.031
wR(F ²)	0.091
Parameters	158
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (eÅ ⁻³)	0.17, -0.12
Crystal size (mm ³)	0.57 × 0.19 × 0.02
Index ranges	-26 ≤ h ≤ 26; -12 ≤ k ≤ 12; -10 ≤ l ≤ 10

Table 2 Atomic Coordinates and Equivalent Isotropic Displacement Parameters for 1.

Atom	X	Y	Z	U_{eq}
O1	0.13541(4)	0.24553(8)	0.21945(9)	0.0246(3)
O2	0.46654(4)	-0.34629(8)	0.92821(9)	0.0318(3)
N1	0.33169(4)	0.02021(8)	0.65633(10)	0.0198(3)
C1	0.17176(5)	0.18925(10)	0.31458(12)	0.0198(3)
C2	0.22814(5)	0.23619(10)	0.35138(11)	0.0198(3)
C3	0.26388(5)	0.17205(10)	0.44657(11)	0.0197(3)
C4	0.24456(5)	0.06010(10)	0.50799(11)	0.0200(3)
C5	0.18816(5)	0.01466(10)	0.47034(12)	0.0217(3)
C6	0.15205(5)	0.07824(11)	0.37561(12)	0.0221(3)
C7	0.28264(5)	-0.01615(10)	0.59873(11)	0.0206(3)
C8	0.36830(5)	-0.07116(11)	0.72306(12)	0.0208(3)
C9	0.40190(5)	-0.03929(11)	0.84216(12)	0.0241(3)
C10	0.43563(5)	-0.12803(12)	0.91434(13)	0.0266(4)
C11	0.43685(5)	-0.24975(11)	0.86471(12)	0.0246(4)
C12	0.40612(5)	-0.28054(11)	0.74038(13)	0.0249(3)
C13	0.37211(5)	-0.19301(10)	0.67067(12)	0.0226(3)
C14	0.49585(6)	-0.32167(14)	1.06057(13)	0.0360(4)

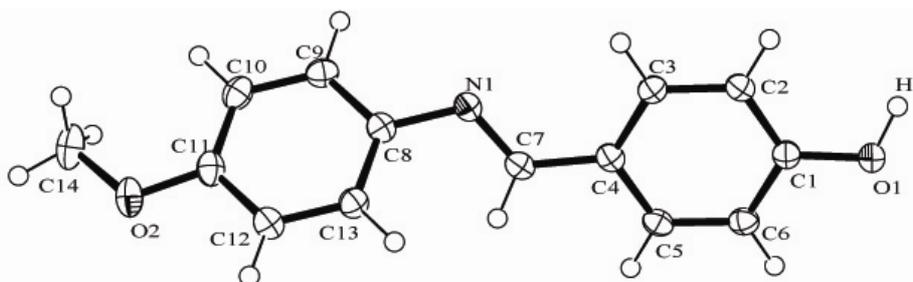
Infrared spectral characteristic

The title compound 1 has a strong band at 1605 cm^{-1} , confirming the presence of the azomethine (C=N) group [11,12]. The stretching frequency at observed at 2838 cm^{-1} show the presence of O-H...N intermolecular hydrogen bond [2]. The spectrum of 1 also shows several weak bands corresponding to aromatic C-H stretching (at $3004\text{--}3067\text{ cm}^{-1}$), aliphatic C-H stretching (at $2863\text{--}2971$

cm^{-1}) and aromatic C-C stretching (at $1503\text{--}1577\text{ cm}^{-1}$) [11,12].

Molecular and crystal structure

The molecular structure of the title compound 1 was determined by single crystal X-ray diffraction and the asymmetric unit is shown in Fig. 1. Bond distances and angles are given in Tables 3 and 4, respectively. Compound 1 crystallizes in the space group Pbcn with one molecule in the asymmetric unit.

**Fig. 1.** Molecular structure of (E)-4-methoxy-N-(4-hydroxybenzylidene)aniline compound, showing 50% probability displacement ellipsoids and the atom-numbering scheme.**Table 3** Bond Distances (Å) for 1.

O1-C1	1.3495(14)	C4-C7	1.4559(15)
O2-C11	1.3681(15)	O2-C14	1.4269(15)
N1-C8	1.4234(14)	N1-C7	1.2839(14)
C1-C2	1.4018(15)	C8-C13	1.4011(16)
C1-C6	1.3944(16)	C9-C10	1.3914(17)
C11-C12	1.3919(17)	C10-C11	1.3886(17)
C2-C3	1.3818(15)	C4-C5	1.3986(16)
C12-C13	1.3749(16)	C8-C9	1.3878(16)
C3-C4	1.4020(15)	C5-C6	1.3808(16)

Table 4 Bond Angles (°) for 1.

N1-C8-C9	119.63(10)	N1-C8-C13	121.75(10)
C11-O2-C14	117.39(10)	N1-C7-C4	125.05(10)
C7-N1-C8	117.82(9)	C9-C8-C13	118.62(10)
O1-C1-C2	122.93(10)	C8-C9-C10	121.00(11)
O1-C1-C6	117.59(10)	C10-C11-C12	119.61(11)
C5-C4-C7	118.62(10)	C11-C12-C13	120.52(11)
C4-C5-C6	121.15(10)	C3-C4-C5	118.34(10)
C3-C4-C7	122.81(10)	C2-C1-C6	119.47(10)
C1-C2-C3	120.00(10)	O2-C11-C10	125.36(10)
C2-C3-C4	120.94(10)	O2-C11-C12	115.03(10)
C9-C10-C11	119.60(11)	C1-C6-C5	120.10(11)

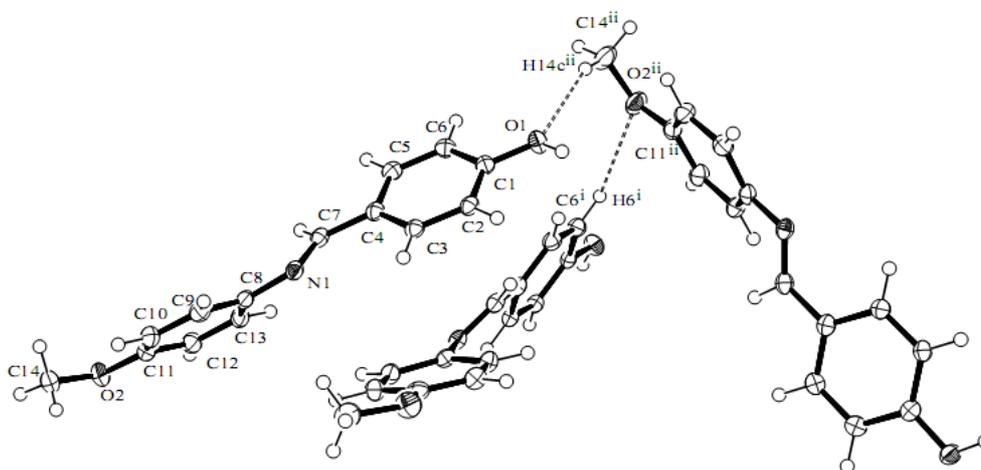
Compound 1 is non-planar, with a dihedral angle between the two aromatic rings of $50.97(32)^\circ$. All bond distances and angles are normal. Bond distances and angles within the aromatic rings are consistent with those expected for sp^2 aromatic carbon atoms and the distance of $C7-C4 = 1.4559(15)$ Å is consistent with single bonds between sp^2 hybridized carbon atoms [11,12]. The bond distances of $N1=C7$ ($1.2839(14)$ Å) and $N1-C8$ ($1.4234(14)$ Å) are consistent with double and

single bonds, respectively [11,12]. The value for the torsion angles of $C8-N1-C7-C4$ is -170.18° .

Strong hydrogen bond $O(1)-H(1)\cdots N(1)$ (Table 5) was found in the structure connecting the molecules into 1D chain running along c . Although the Structure contains only one symmetry independent molecule the packing of the 1D chain is complicated (see Fig. 2) due to high symmetry. No strong interaction exists between the chains.

Table 5 Hydrogen-bond geometry (Å, °).

D-H...A	D-H	H...A	D...A	D-H...A
$O1\cdots H14c^{ii}\cdots C14^{ii}$	0.960	2.493	3.371	151.966
$O2^{ii}\cdots H6^i\cdots C6^i$	0.960	2.883	3.675	140.420

**Fig 2** Crystal structure of 1. Inter-molecular hydrogen bonds are shown as a dashed line.

Supplementary data

Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Center, CCDC Nos. 761896. 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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References

- [1] Khalaji A.D., Mighani H., Gotoh K., Ishida H., "Synthesis, characterization, structure, *Ab initio* and DFT calculations of 2-Amino-N-(3-phenylprop-2-enylidene)aniline", J. Chem. Cryst. 41 (2011) 1154-1157.
- [2] Khalaji A.D., Mighani H., Bijanzadeh H.R., Gotoh K., Ishida H., "One dimensional hydrogen bonded arrangement in new Schiff-base compound (*E*)-2-(2,5-dimethoxybenzylideneamino)phenol (1): Synthesis, characterization", crystal structure and conformational studies, J. Chem. Cryst. 41 (2011) 1515-1519.
- [3] van der Anker T.R., Cave G.W.V., Raston C.L., "Benign approaches for the synthesis of bis-imine Schiff bases", Green Chem. 8 (2006) 50-53.
- [4] Hamaker C.G., Maryashina O.S., Daley D.K., Wadler A.L., "Synthesis and crystal structure of two Schiff bases of 2-(methylthio)aniline with halogenated salicylaldehydes", J. Chem. Cryst. 40 (2010) 34-39.
- [5] Hijji Y.M., Barare B., Kennedy A.P., Butcher R., "Synthesis and photophysical characterization of a Schiff base as anion sensor", Sensors & Actuators B136 (2009) 297-301.
- [6] Hadjoudis E., Ronroyianni A., Ambroziak K., Dziembowska T., Mavridis I.M., "Photochromism

and thermochromism of solid *trans*-N,N'-bis-(salicylidene)-1,2-cyclohexanediamines and *trans*-N,N'-bis-(2-hydroxy-naphylidene)-1,2-cyclohexanediamine", J. Photochem. Photobiol. A162 (2004) 521-530.

[7] Karakas A., Unver H., Elmali A., "Synthesis, structure, linear and third-order nonlinear optical behavior of N-(3-hydroxybenzalidene)-4-bromoaniline", J. Mol. Struct. 877 (2008) 152-157.

[8] Karakas A., Elmali A., Unver H., "Nonlinear optical properties, synthesis, structures and spectroscopic studies of N-(4-nitrobenzylidene)-o-fluoroamine and N-(3-nitrobenzylidene)-p-fluoroamine", Spectrochim. Acta A61 (2005) 2979-2987.

[9] Aslantas M., Kendi E., Demir N., Sabik A.E., Tumer M., Kertmen M., "Synthesis, spectroscopic, structural characterization, electrochemical and antimicrobial activity studies of the Schiff base ligand and its transition metal complexes", Spectrochim. Acta A74 (2009) 617-624.

[10] Unver H., Yildiz M., Dulger B., Ozgen O., Kendi E., Durlu T.N., "Spectroscopic studies, antimicrobial activities and crystal structures of N-(2-hydroxy-3-methoxybenzalidene)-1-aminonaphthalene", J. Mol. Struct. 737 (2005) 159-164.

[11] Khalaji A.D., Najafi Chermahini A., Fejfarova K., Dusek M., "Synthesis, characterization, crystal structure, and theoretical studies on Schiff base compound 6-[(5-bromopyridin-2-yl)iminomethyl]phenol", Struct. Chem. 21 (2010) 153-157.

[12] Khalaji A.D., Fejfarova K., Dusek M., "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", Acta Chim. Slov. 57 (2010) 257-261.

[13] Khalaji A.D., Fejfarova K., Dusek M., "Synthesis and crystal structure of Schiff base compounds N-(3,4-dimethoxybenzylidene)-4-methoxyaniline (1) and N-(3,4-

dimethoxybenzylidene)-4-ethoxyaniline (2)", J. Cryst. Miner. 19 (2011) 41-46.

[14] Burla M.C., Camalli M, Carrozzini B, Cascarano G, Giacovazzo C, Polidori G, Spagna R, SIR2002 : the program, J. Appl. Cryst. 36 (2003) 1103.

[15] Petricek V, Dusek M, Palatinus L., Jana2006., "Structure determination software programs", Institute of Physics, Praha, Czech Republic (2008).

[16] Farrugia L.J., "ORTEP-3 for Windows - a version of ORTEP-III with a Graphical User Interface (GUI)", J. Appl. Cryst. 30 (1997) 565.