

Synthesis and Crystal Structure of Schiff-base Compounds N-(3, 4-dimethoxybenzylidene)-4-methoxyaniline (1) and N-(3, 4-dimethoxybenzylidene)-4-ethoxyaniline (2)

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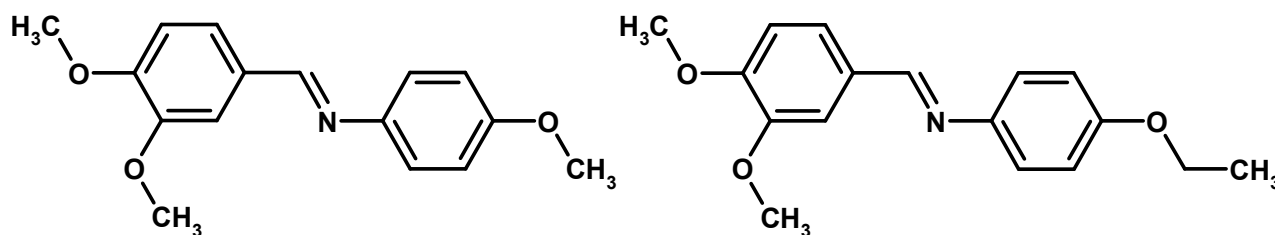
Abstract: New Schiff-base compounds N-(3,4-dimethoxybenzylidene)-4-methoxyaniline (1) and N-(3,4-dimethoxybenzylidene)-4-ethoxyaniline (2) were synthesized and characterized by elemental analyses (CHN) and FT-IR spectroscopic techniques. Crystal structures of 1 and 2 were obtained by single-crystal X-ray diffraction. Compound 1 crystallizes in the monoclinic, space group $P2_1$ with two independent molecules (A and B), with unit cell parameters: $a = 14.8198(4)$, $b = 7.1656(2)$, $c = 13.2982(4)$ Å, $\beta = 103.289(2)^\circ$, $V = 1374.36(7)$ Å³ and $Z = 4$ and compound 2 crystallizes in the monoclinic space group $P2_1/n$ with unit cell parameters: $a = 16.5638(6)$, $b = 7.3546(2)$, $c = 12.7449(4)$ Å, $\beta = 106.021(4)^\circ$, $V = 1492.28(9)$ Å³ and $Z = 4$.

Keywords: Schiff-base; crystal structure; monoclinic.

Introduction

German chemist, Hugo Schiff, developed a new class of organic compounds, with an imine group ($-C=N-$) and benzene ring, known as Schiff-base in his honor [1]. The preparation of these compounds is simple. They are prepared by condensing an aldehyde with an amine, generally at room temperature or in refluxing alcohol [2], and are often used as ligands in coordination chemistry [3]. These compounds have been studied for their use as anion sensors [4], antimicrobial activity [5],

photochromism and thermochromism [6] and nonlinear optical properties [7]. In recent years, we have been interested in Schiff-base complexes [8, 9]. As a continuation of our previous works [10, 11], Schiff-base compounds N-(3, 4-dimethoxybenzylidene)-4-methoxyaniline (1) and N-(3, 4-dimethoxybenzylidene)-4-ethoxyaniline (2) (Scheme 1) were synthesized and characterized by elemental analyses, FT-IR and X-ray crystallography.



Scheme 1 The Schiff bases compounds 1 (left) and 2 (right)

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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. The infrared spectra were recorded on a Perkin Elmer spectrophotometer as a KBr pellet.

Preparation of 1 and 2

3,4-Dimethoxybenzaldehyde (0.4 mmol) and corresponding amines (4-methoxyaniline for 1 and 4-ethoxyaniline for 2) (0.2 mmol) were dissolved in methanol (25 ml) at room temperature. The mixture was stirred and heated for 30 min to give a clear solution. After keeping the solution in air for 5 days for 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. Colorless, Yield: 85%. Anal. Calc. for $C_{16}H_{17}NO_3$: C 70.83, H 6.31, N 5.16; found: C 70.75, H 6.24, N 5.20. IR (KBr): 2838-3009 (m, C-H aromatic and aliphatic), 1621 (s, C=N), 1508-1602 (C=C aromatic). Compound 2. Colorless, Yield: 83%. Anal. Calc. for $C_{17}H_{19}NO_3$: C 71.55, H 6.71, N 4.91; found: C 71.67, H 6.69, N 4.85. IR (KBr): 2829-2999 (m, C-H aromatic and aliphatic), 1619 (s, C=N), 1509-1601 (C=C aromatic).

X-ray structure determination

Single crystals with the dimensions 0.74 mm ×

0.20 mm × 0.05 mm of 1 and 0.33 mm × 0.23 mm × 0.11 mm of 2 were chosen for 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 structures were solved by direct methods with program SIR2002 [12] and refined with the Jana2006 program package [13] by full-matrix least-squares technique on F^2 . The molecular structure plots were prepared by ORTEP-3 [14]. 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 Crystallographic data (excluding structure factors) for the structure reported in this research has been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 772110 for 1 and 772111 for 2. 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>.

Table 1 Crystal and Refinement Data for compounds 1 and 2.

	1	2
Formula	$C_{16}H_{17}NO_3$	$C_{17}H_{19}NO_3$
M_r [g/mol]	271.3	285.3
Crystal system, space group	Monoclinic, $P2_1$	Monoclinic, $P2_1/n$
Unit cell dimensions [\AA , °]:	$a = 14.8198(4)$ $b = 7.1656(2)$ $c = 13.2982(4)$ $\beta = 103.289(2)$	$a = 16.5638(6)$ $b = 7.3546(2)$ $c = 12.7449(4)$ $\beta = 106.021(4)$
V [\AA^3]	1374.36(7)	1492.28(9)
Z	4	4
D_x [g cm^{-3}]	1.3108	1.2696
μ [mm^{-1}]	0.75	0.71
$F(000)$	576	608
Temperature (K)	120	120
Absorption correction	Multi scan ($T_{\min} = 0.692$, $T_{\max} = 1.000$)	Multi scan ($T_{\min} = 0.529$, $T_{\max} = 1.000$)
Index ranges	$-15 \leq h \leq 17$ $-8 \leq k \leq 8$ $-15 \leq l \leq 15$	$-18 \leq h \leq 18$ $-8 \leq k \leq 8$ $-14 \leq l \leq 14$
Nref, Npar refined	2559, 361	25918, 190
R_{int}	0.029	0.064
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$	0.034, 0.092	0.046, 0.125
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e \AA^{-3})	0.19, -0.15	0.21, -0.25

Results and Discussion

Synthesis and characterization

Both compounds 1 and 2 were obtained in relatively high yields, 85% and 83% respectively. The stability of dissolved compounds is much lower than in the solid state and depends on the nature of the solvent. The title compounds are very slightly soluble in common organic solvents such as acetonitrile and methanol but completely soluble in chloroform and dichloromethane. The strong bands at 1621 cm^{-1} for 1 and 1619 cm^{-1} for 2 in their respective FT-IR spectra are assigned to the C=N stretching vibration. The FT-IR spectra of 1 and 2 also show several weak bands corresponding to aromatic and aliphatic C-H stretching ($2838\text{--}3009\text{ cm}^{-1}$ for 1 and $2829\text{--}2999\text{ cm}^{-1}$ for 2), and

aromatic C-C stretching ($1508\text{--}1602\text{ cm}^{-1}$ for 1 and $1509\text{--}1601\text{ cm}^{-1}$ for 2) [10,11].

Molecular and crystal structure

The molecular structures of compounds 1 and 2 with the atom numbering scheme shown in Figures 1 and 2, respectively, are not planar. Selected bond distances and angles (Tables 2 and 3) are normal and are in good agreement with those reported in similar Schiff-base compounds. The C9=N1 and C25=N2 bond lengths of $1.276(2)$ and $1.281(2)\text{ Å}$, respectively, in 1 and C9=N1 bond length of $1.278(2)\text{ Å}$, in 2, conforms to the value for a double bond, while C10-N1 and C26-N2 bond lengths of $1.420(3)$ and $1.417(3)\text{ Å}$, respectively, in 1 and C10-N1 bond length of $1.418(3)\text{ Å}$, in 2, conforms to the value for a single bond, like in similar Schiff-base compounds [10,11].

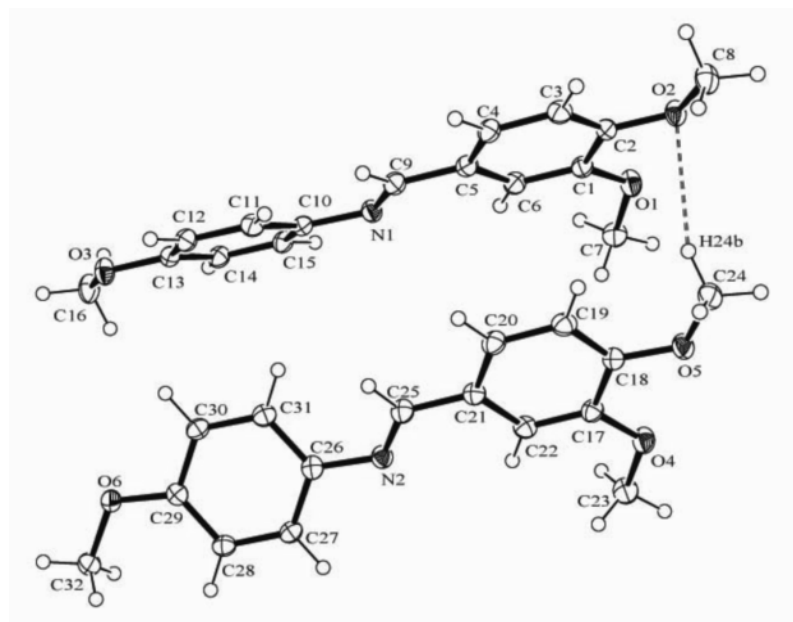


Figure 1 An ortep view of 1, showing 50% probability displacement ellipsoids and the atom numbering scheme. The C-H...O hydrogen bond is indicated by dashed line.

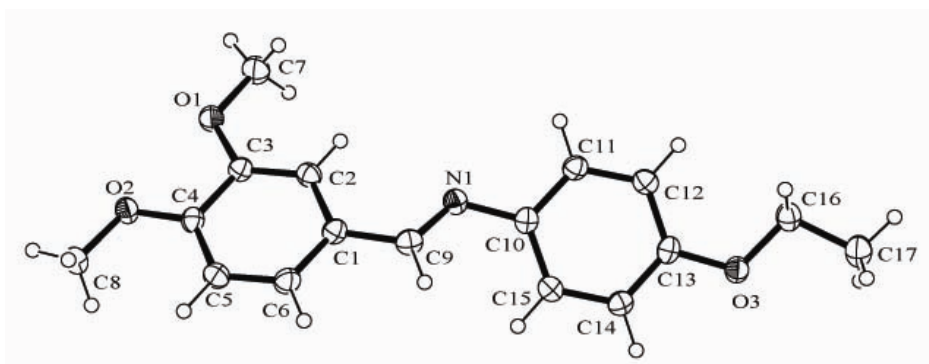


Figure 2 An ortep view of 2, showing 50% probability displacement ellipsoids and the atom numbering scheme.

Table 2 Selected bond lengths (in Å) and angles (in °) for 1.

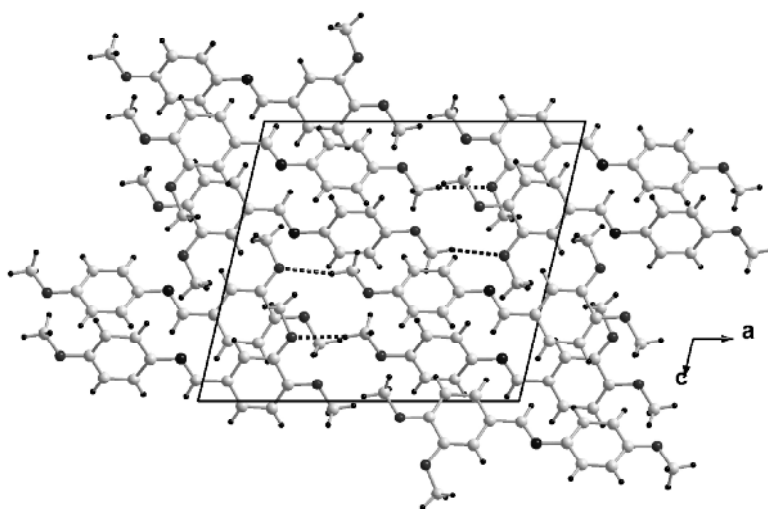
O1-C1	1.365(2)	O5-C18	1.361(2)	N2-C25	1.281(2)
O1-C7	1.439(2)	O5-C24	1.434(2)	N2-C26	1.417(3)
O2-C2	1.363(2)	O6-C29	1.367(2)	N1-C9	1.276(2)
O2-C8	1.432(2)	O6-C32	1.435(2)	N1-C10	1.420(3)
O3-C13	1.368(2)	O4-C17	1.362(2)	O4-C23	1.429(2)
O3-C16	1.435(3)				
C1-O1-C7	116.70(14)	C9-N1-C10	120.70(18)	N1-C9-C5	123.4(2)
C2-O2-C8	117.65(16)	C25-N2-C26	119.16(17)	N1-C10-C11	125.62(18)
C13-O3-C16	117.32(17)	O1-C1-C2	114.60(17)	N1-C10-C15	116.43(19)
C17-O4-C23	116.72(14)	O1-C1-C6	125.36(16)	N2-C25-C21	123.59(18)
C18-O5-C24	117.12(15)	O2-C2-C1	115.48(18)	N2-C26-C27	118.24(19)
C29-O6-C32	117.69(17)	O2-C2-C3	124.81(16)	N2-C26-C31	123.31(18)
O3-C13-C14	124.69(17)	O4-C17-C22	125.54(15)	O6-C29-C30	115.35(19)
O3-C13-C12	115.72(19)	O5-C18-C17	114.80(17)	O6-C29-C28	125.19(18)
O4-C17-C18	114.43(16)	O5-C18-C19	125.41(15)		

Table 3 Selected bond lengths (in Å) and angles (in °) for 2.

O1-C3	1.374(2)	O3-C13	1.374(3)
O1-C7	1.425(2)	O3-C16	1.431(2)
O2-C4	1.356(3)	N1-C9	1.278(2)
O2-C8	1.432(2)	N1-C10	1.418(3)
C3-O1-C7	117.24(16)	N1-C9-C1	123.39(17)
C4-O2-C8	117.35(14)	N1-C10-C11	117.75(16)
C13-O3-C16	117.56(14)	N1-C10-C15	124.07(16)
O1-C3-C2	125.46(16)	O2-C4-C3	115.62(16)
O1-C3-C4	114.00(17)	O2-C4-C5	125.25(17)
O3-C13-C14	115.81(16)	O3-C16-C17	107.47(15)
C9-N1-C10	119.71(16)		

The bond angles C10-N1-C9, C26-N2-C25 in 1 and C9-N1-C10 bond angles in 2 are 120.70(18), 119.16(17) and 119.71(16)°, respectively, which is consistent with the sp^2 hybrid character of N atoms. In the packing diagrams for compounds 1

and 2, molecules are stabilized by intermolecular hydrogen bonding that occur between C-H...O atoms of neighboring molecules (Figs. 3 and 4, Tables 4 and 5).

**Figure 3** Packing diagram of 1.

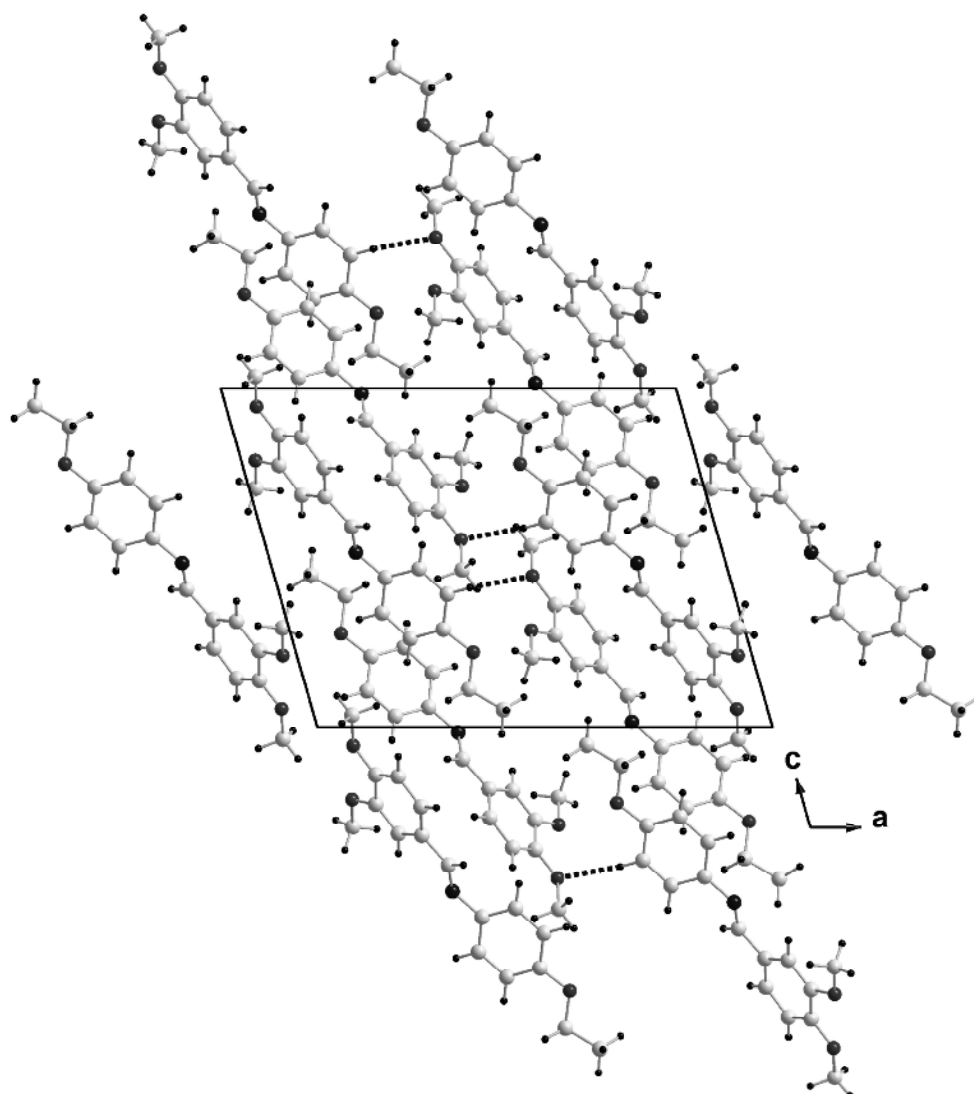


Figure 4 Packing diagram of 2.

Table 4 Hydrogen-Bonding parameters for 1.

D-H...A	D-H [Å]	A...H [Å]	D...A [Å]	D-H...A [°]
C16-H16A...O1	0.960	2.48	3.422(3)	168
C16-H16A...O2	0.960	2.60	3.297(2)	130
C32-H32A...O4	0.960	2.59	3.513(3)	161

Table 5 Hydrogen-Bonding parameters for 2.

D-H...A	D-H [Å]	A...H [Å]	D...A [Å]	D-H...A [°]
C8-H8C...O1	0.960	2.54	3.478(2)	164
C14-H14...O2	0.960	2.39	3.332(2)	166

Acknowledgements

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References

- [1] Carry F.A., Organic Chemistry., 5th edn. McGraw-Hill, New York, (2003) 724.
- [2] Jarzabek B., Kaczmarczyk B., Sek D., Spectrochim. Acta. A74 (2009) 949.
- [3] Dolaz M., McKee V., Golcu A., Tumer M., "Spectrochim. Acta." A71 (2009) 1648.
- [4] Hijji Y.M., Barare B., Kennedy A.P., Butcher R., "Sensors & Actuators." B136 (2009) 297.
- [5] Aslantas M., Kendi E., Demir N., Sabik A.E., Tumer M., Kertmen M., Spectrochim. Acta. A74 (2009) 617.
- [6] Hadjoudis E., Rontoyianni A., Ambroziak K., Aziembowska T., Mavridis I.M., J. Photochem. Photobiol. A162 (2004) 521.
- [7] Karakas A., Unver H., Elmali A., J. Mol. Struct. 877 (2008) 152.
- [8] Khalaji A.D., Weil M., Hadadzadeh H., Daryanavard M., Inorg. Chim. Acta. 362 (2009) 4837.
- [9] Khalaji A.D., Hadadzadeh H., Fejfarova K., Dusek M., Polyhedron 29 (2010) 807.
- [10] Khalaji A.D., Najafi Chermahini A., Fejfarova K., Dusek M., Struct. Chem. 21 (2010) 153.
- [11] Khalaji A.D., Fejfarova K., Dusek M., Acta Chim. Slov. 57 (2010) 257.
- [12] Burla M.C., Camalli M., Carrozzini B., Cascarano G., Giacovazzo C., Polidori G., Spagna R., SIR2002: the program, J. Appl. Cryst. 36 (2003) 1103.
- [13] Petricek V., Dusek M., Palatinus L., Jana2006. "Structure determination software programs. Institute of Physics", Praha, Czech Republic (2008).
- [14] Farrugia L.J., J. Appl. Cryst. 30 (1997) 565.