

КРАТКИЕ СООБЩЕНИЯ

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MOLECULAR AND CRYSTAL STRUCTURE OF
(*E*)-4-CHLORO-*N*-(3,4-DIMETHOXYBENZYLIDENE)ANILINE© 2011 A.D. Khalaji¹*, K. Fejfarova², M. Dusek²¹Department of Chemistry, Faculty of Science, Golestan University, Gorgan, Iran²Institute of Physics of the ASCR, v.v.i., Na Slovance 2, 182 21 Prague 8, Czech Republic

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The reaction of 3,4-dimethoxybenzaldehyde with 4-chloroaniline (1:1 molar ration) leads to the formation of a new Schiff base (*E*)-4-chloro-*N*-(3,4-dimethoxybenzylidene)aniline (**1**) that is successfully obtained and characterized by elemental analyses, FT-IR and ¹H NMR spectroscopy, and single crystal X-ray diffraction. The strong absorption band at 1620 cm⁻¹ in the FT-IR spectrum and a singlet signal at 8.32 ppm in the ¹H NMR spectrum of **1** clearly proves the presence of the C=N (azomethine) group. Single crystal X-ray analyses reveal that the title compound adopts an *E* configuration with respect to the C=N bond.

Key words: single crystals, grown, spectroscopy, crystallography.

Organic materials, such as Schiff bases and triazines, have received a great deal of attention in the recent years due to their NLO properties [1, 2], biological activity [3] and anti-HIV effect [4, 5]. Schiff base compounds as an important class of organic materials that show good crystallizability have been extensively studied as corrosion inhibitors for steel and iron [6—9]. In the recent years, we have reported the crystal structures of several Schiff base compounds [10—13]. In this work, we describe the crystal structure of the Schiff base compound (*E*)-4-chloro-*N*-(3,4-dimethoxybenzylidene)aniline (**1**).

Experimental. All reagents (3,4-methoxybenzaldehyde and parachloroaniline) and solvents (methanol and chloroform) for synthesis, crystal 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. The ¹H 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 spectrum was recorded on a JASCO 680 plus FT-IR spectrophotometer as a KBr pellet.

A solution of 4-chloroaniline (1.27 g, 0.1 mol) in 10 ml of methanol was heated for 10 min. To this solution a hot solution of 3,4-dimethoxybenzaldehyde (1.65 g, 0.1 mol) in 40 ml of methanol was added dropwise with constant stirring. The mixture was heated for 2 h and then allowed to cool overnight at 273 K. The resulting crude solid was collected by filtration and dried at room temperature. The solubility of **1** was determined by adding the solvent to a known amount of the compound until completely dissolved. It was found that the synthesized compound was moderately soluble in methanol, ethanol, and acetonitrile, insoluble in water and completely soluble in chloroform, dichloromethane, and *N,N*-dimethylformamide (DMF). Crystals were grown by the slow evaporation technique at room temperature using a mixture of 25 ml of chloroform-methanol (5:1 v/v) as a solvent. At the period of super saturation, tiny crystals nucleated. They were allowed to grow to a maximum possible size and then filtered. Yield: 88 %. *Anal.* Calc. for C₁₅H₁₄ClNO₂: C, 65.33; H, 5.12; N, 5.08 %. Found: C, 65.29; H, 5.08; N, 5.10 %.

* E-mail: alidkhalaji@yahoo.com

Table 1

Crystal data and summary of experimental details for compound 1

Empirical formula	C ₁₅ H ₁₄ CINO ₂	Measured reflections	14671
Formula weight	275.7	Independent reflections	4210
Crystal system	Monoclinic	Reflection with $I > 3\sigma(I)$	3689
Space group	$P2_1/c$	R_{int}	0.019
T , K	120	$R[F^2 > 3\sigma(F^2)]$	0.028
a, b, c , Å	12.4616(4), 7.2252(2), 30.0144(6)	$wR(F^2)$	0.082
β , deg.	96.111(2)	Parameters	344
V , Å ³	2687.07(13)	$\Delta\rho_{\text{max}}$, eÅ ⁻³	0.15
Z	8	$\Delta\rho_{\text{min}}$, eÅ ⁻³	-0.13
μ , mm ⁻¹	2.50	Crystal size, mm ³	0.34×0.23×0.06
T_{min}	0.413	Index ranges	$-13 \leq h \leq 14, -8 \leq k \leq 8,$
T_{max}	0.863		$-34 \leq l \leq 32$

A single crystal of the title compound with the dimensions of 0.34×0.23×0.06 mm was chosen for the X-ray diffraction study. Crystallographic measurements were made with a four circle CCD Gemini diffractometer (Oxford diffraction, Ltd.) with mirrors-collimated CuK α radiation ($\lambda = 1.54184$ Å). The crystal structure was solved by direct methods using the SIR2002 program [14] and refined using the Jana2006 program package [15] by the 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 $1.2U_{\text{eq}}$ of the parent atom. Crystallographic data and details of the data collection and structure refinements are listed in Table 1.

Characterization. In order to confirm the chemical composition of the synthesized compound, CHN analysis was carried out on the recrystallized sample using a Heraeus CHN-O-Rapid analyzer. The result of the analysis is presented in the experimental section. Theoretical values of CHN have suggested the molecular formula C₁₅H₁₄CINO₂. The experimental and calculated values of C, H, and N agree to each other, confirming the formation of C₁₅H₁₄CINO₂.

The ¹H NMR spectra of (*E*)-4-chloro-*N*-(3,4-dimethoxybenzylidene)aniline (Fig. 1) display two singlet signals at 3.94 and 3.97 ppm that are assigned to protons of the methoxy groups, H_g and H_h, respectively; one doublet signal at 6.92 ppm assigned to the aromatic H_e proton; one doublet signal at 7.13 ppm assigned to aromatic H_a protons; one doublet of doublet signal at 7.29 ppm assigned to aromatic H_d protons; one doublet signal at 7.33 ppm assigned to aromatic H_b protons; one singlet signal at 7.60 ppm assigned to aromatic H_f protons; and one singlet signal at 8.32 ppm assigned to the C=N group (H_c).

The FT-IR analysis of **1** was carried out to investigate the presence of functional groups and their vibrational modes. The sample was prepared in the form of a pellet by mixing **1** with KBr. The spectrum was recorded between 400 and 4000 cm⁻¹ using a JASCO 680 plus FT-IR spectrophotometer. The FT-IR spectrum confirms the formation of **1** and its characteristic frequencies. Relatively weak absorption bands around 2800–3000 cm⁻¹ observed in the IR spectra are assigned to the C–H vibrational modes involving the aromatic and aliphatic hydrogen atoms. The absorption bands with a variable intensity around 1400–1600 cm⁻¹ correspond to the vibrations of the aromatic rings of the ligand. The strong and sharp stretching vibration at 1620 cm⁻¹ is assigned to $\nu(\text{C}=\text{N})$.

Crystal structure description. The molecular structure of the title compound with the atom numbering scheme is given in Fig. 2. Selected bond distances and angles (Table 2) are in good agreement with those reported in similar Schiff base compounds [10–14].

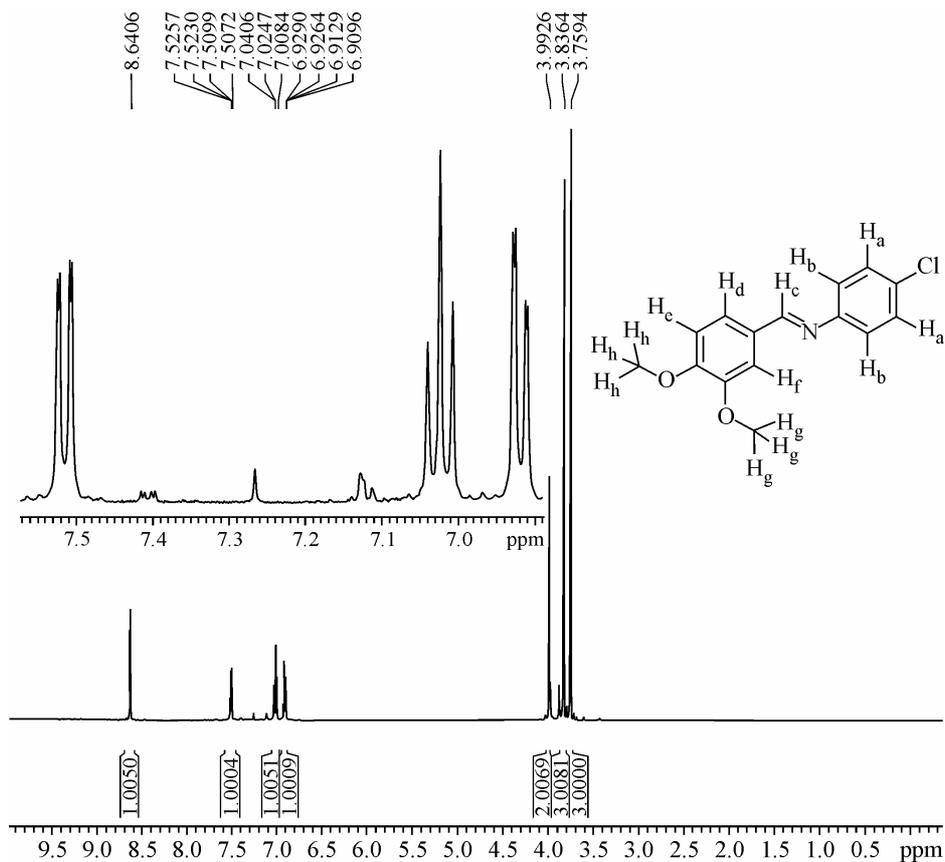


Fig. 1. ^1H NMR spectrum of **1**

The C(7)=N(1) and C(22)—N(2) bond lengths of 1.2775(17) and 1.2800(16) Å respectively conform to the value for a double bond and are similar to the corresponding bond length in **1**, C(1)=N(7) 1.288(7) Å [14], and slightly longer than in 4-bromo-*N*-(3,4,5-trimethoxybenzylidene) aniline, C(7)=N(1) 1.268(3) Å [12]. The C(8)—N(1) and C(23)—N(2) bond lengths of 1.4138(17) and

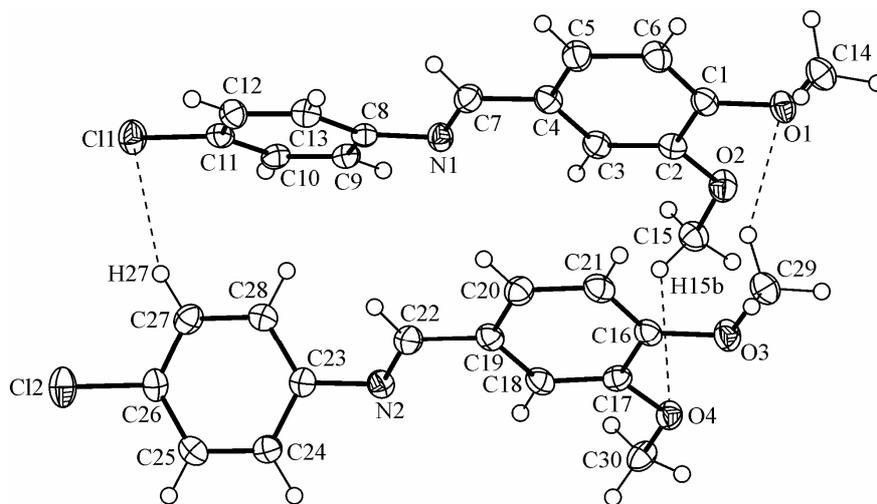


Fig. 2. Structure of **1** with 50 % probability displacement ellipsoids and atomic numbering. Dashed lines represent C—H...O and C—H...Cl hydrogen bonds

Table 2

Selected bond distances (Å) and angles (deg.) for compound 1

Cl(1)—C(11)	1.7428(14)	N(1)—C(7)	1.2775(17)	O(4)—C(17)	1.3656(15)
O(1)—C(1)	1.3598(16)	N(1)—C(8)	1.4138(17)	O(4)—C(30)	1.4270(15)
O(1)—C(14)	1.4352(15)	Cl(2)—C(26)	1.7437(14)	N(2)—C(22)	1.2800(16)
O(2)—C(2)	1.3611(15)	O(3)—C(16)	1.3572(16)	N(2)—C(23)	1.4134(17)
O(2)—C(15)	1.4272(15)	O(3)—C(29)	1.4321(15)		
C(1)—O(1)—C(14)	117.58(10)	O(1)—C(1)—C(2)	114.46(11)	C(22)—N(2)—C(23)	119.71(11)
C(2)—O(2)—C(15)	116.97(10)	O(1)—C(1)—C(6)	125.78(11)	N(2)—C(22)—C(19)	122.54(12)
Cl(1)—C(11)—C(10)	119.41(10)	O(2)—C(2)—C(1)	114.82(11)	N(2)—C(23)—C(24)	117.63(11)
Cl(1)—C(11)—C(12)	119.25(10)	O(2)—C(2)—C(3)	125.47(11)	N(2)—C(23)—C(28)	123.20(11)
C(7)—N(1)—C(8)	121.06(11)	C(16)—O(3)—C(29)	117.03(10)	O(3)—C(16)—C(17)	114.52(11)
N(1)—C(7)—C(4)	122.74(12)	C(17)—O(4)—C(30)	116.84(10)	O(3)—C(16)—C(21)	125.83(11)
N(1)—C(8)—C(9)	116.34(11)	Cl(2)—C(26)—C(25)	119.24(10)	O(4)—C(17)—C(16)	114.79(11)
N(1)—C(8)—C(13)	125.37(11)	Cl(2)—C(26)—C(27)	119.13(11)	O(4)—C(17)—C(18)	125.15(11)

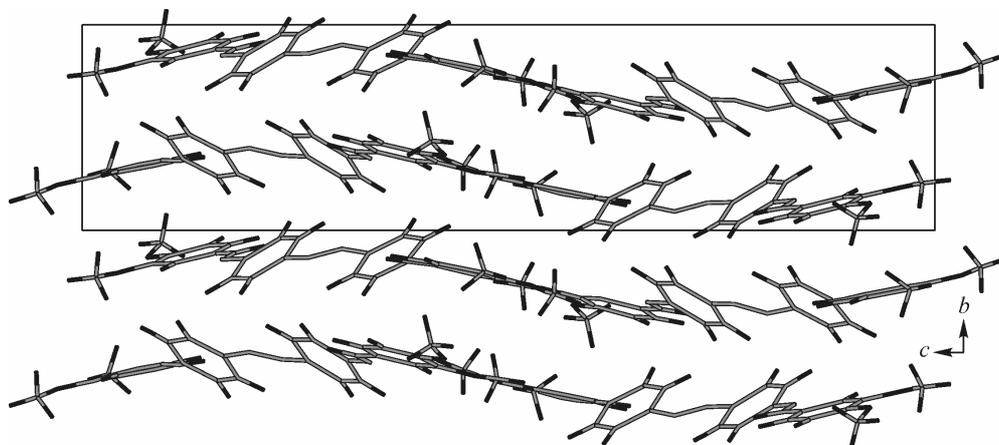
1.4134(17) Å conform to the value for a single bond, and in turn are similar to the corresponding bond length in (*E*)-4-bromo-*N*-(2,4-dimethoxybenzylidene) aniline, C(10)—N(1) 1.417(7) Å [14], and are slightly shorter than the corresponding bond length in 4-bromo-*N*-(3,4,5-trimethoxybenzylidene) aniline, C(4)—N(1) 1.421(2) Å [12]. All other bond lengths in the three related Schiff base compounds are quite similar. The torsion angles of the title compound, C(8)—N(1)—C(7)—C(4) and C(23)—N(2)—C(22)—C(19), are 179.078(118) and $-178.411(112)^\circ$ respectively, indicating an almost planar *E*-configuration with respect to the imine C=N bond [10–14]. The two independent molecules interact with each other *via* extremely weak H-bonds C(29)—H(29b)⋯O(1), C(15)—H(15b)⋯O(4) and C(27)—H(27)⋯Cl(1) (Fig. 2 and Table 3).

In a view along *a*, there are warped slabs between the neighboring molecules of this compound (Fig. 3). There are no Cl—Cl interactions in the slabs along the *a* axis, while short Cl—Cl interactions occur only in the two neighboring slabs projected along *b* (Fig. 4). From this figure it is clear that nei-

Table 3

Hydrogen-bonds geometry (Å, deg.) for compound 1

<i>D</i> —H⋯ <i>A</i>	<i>D</i> —H	H⋯ <i>A</i>	<i>D</i> ⋯ <i>A</i>	<i>D</i> —H⋯ <i>A</i>
C(29)—H(29b)⋯O(1)	0.960	2.697	3.498	141.317
C(15)—H(15b)⋯O(4)	0.960	2.887	3.643	136.454
C(27)—H(27)⋯Cl(1)	0.960	3.056	3.920	150.529

Fig. 3. Warped slabs between the neighboring molecules of compound 1 along the *a* axis

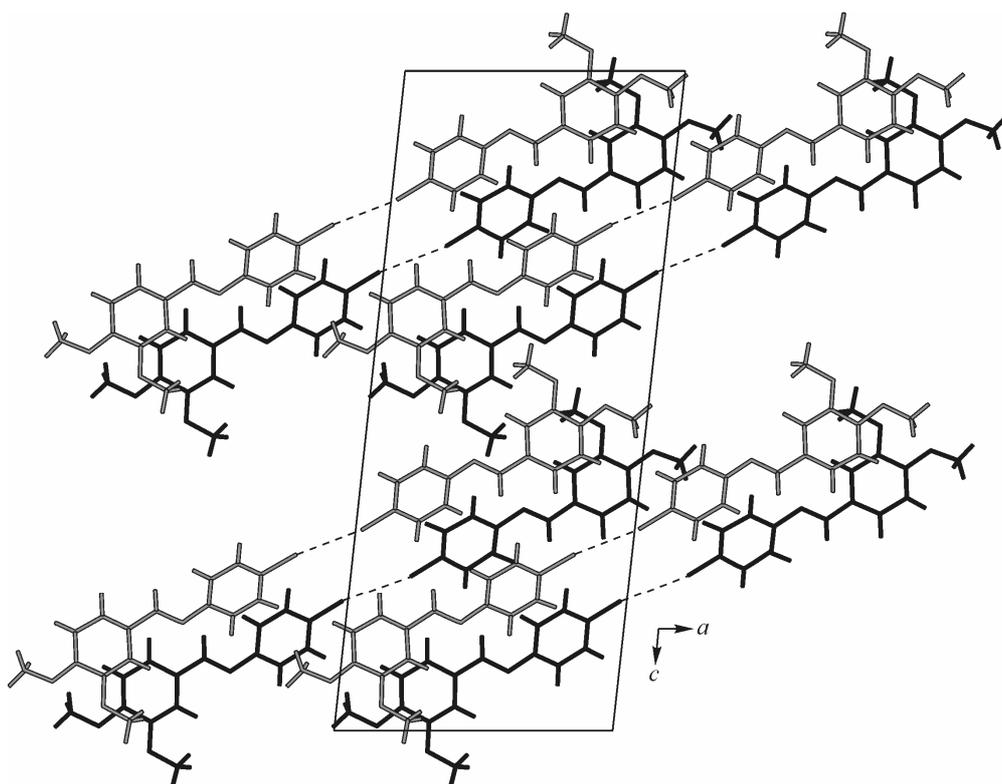


Fig. 4. Cl—Cl interactions occur in the two neighboring slabs projected along the *b* axis

ther C—H...O hydrogen bonds nor π — π interactions could cause attraction between the molecules in the slab that would shorten the Cl—Cl distance. Thus, the short distance seems to be caused solely by space requirements of the molecular packing [18, 19].

Conclusions. A new Schiff base compound (*E*)-4-chloro-*N*-(3,4-dimethoxybenzylidene)aniline (**1**) was synthesized, and the single crystals of this compound were successfully grown by the solution growth technique at room temperature using a mixture of 25 ml of chloroform-methanol (5:1 *v/v*) as a solvent. FT-IR spectroscopy have confirmed the functional groups, particularly the —HC=N imine group, in the title compound. The single crystal X-ray diffraction study of the monoclinic crystals has revealed two symmetry independent molecules of normal geometry.

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Appendix. Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Center, CCDC No. 729837. 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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