Crystal Structures of New Schiff Bases *N,N'*-Bis(2-hydroxy-3-methoxybenzylidene)-1,4-diaminobutane and *N,N'*-Bis(2-hydroxy-4-methoxybenzylidene)-1,2-diaminoethane

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The crystal structures of *N, N'*-bis(2-hydroxy-3-methoxybenzylidene)-1,4-diaminobutane (**1**) and *N, N'*-bis (2-hydroxy-4-methoxybenzylidene)-1,2-diaminoethane (**2**) have been determined by single-crystal X-ray diffraction. Compound **1** crystallizes in the triclinic space group $P\bar{1}$ with a = 12.6062(15), b = 12.6317(14), c = 12.8917(15) Å, α = 102.728(2), β = 110.493(2), γ = 92.266(2)°, Z = 4, with 4 crystallographically independent molecules in the unit cell, each having crystallographic inversion symmetry. Compound **2** crystallizes in the monoclinic space group $C2/c$ with a = 18.840(4), b = 7.6120(18), c = 11.5311(11) Å, β = 90.379(17)°, Z = 4. The molecules have crystallographic C_2 symmetry. Intramolecular hydrogen bonds occur between O(2) and N(1) (2.597(2) Å) and between O(4) and N(2) (2.588(2) Å) for **1** (values for two independent molecules), and between O(1) and N(1) (2.587 (2) Å) for **2**.

Key words: Schiff Base, X-Ray Structure

Introduction

Schiff base ligands are able to coordinate metals through imine nitrogen atoms and other groups, usually linked to the aldehyde. Modern chemists still prepare Schiff bases, and nowadays active and well-designed Schiff base ligands are considered 'privileged ligands' [1]. Schiff bases are an important class of ligands in coordination chemistry and their metal complexes play a key role in understanding the coordination chemistry of transition metal ions. Schiff base metal complexes have widely been studied because of their industrial, antifungal, anticancer, and many other applications in biology. For example, salen and benzylidene-type ligands are the oldest class of ligands in coordination chemistry [2 – 6]. 2-Hydroxy Schiff base ligands and their complexes derived from the reaction of salicylaldehyde and 2-hydroxy-1-naphthaldehyde with amines have been studied extensively [7 – 11].

Table 1. Crystal structure data for **1** and **2**.

	1	**2**
Formula	$C_{20}H_{24}N_2O_4$	$C_{18}H_{20}N_2O_4$
M_r	356.41	328.36
Cryst. size [mm^3]	0.40×0.40×0.12	0.45×0.40×0.30
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$C2/c$
a [Å]	12.6062(15)	18.840(4)
b [Å]	12.6317(14)	7.6120(18)
c [Å]	12.8917(15)	11.5311(11)
α [deg]	102.728(2)	90
β [deg]	110.493(2)	90.379(17)
γ [deg]	92.266(2)	90
V [Å^3]	1860.3(4)	1653.6(5)
Z	4	4
D_{calcd} [g cm^{-3}]	1.273	1.319
μ(MoK_α) [cm^{-1}]	0.089	0.094
F(000) [e]	760	696
hkl range	$-16 \le h \le 16$	$-24 \le h \le 23$
	$-16 \le k \le 16$	$-9 \le k \le 9$
	$-16 \le l \le 16$	$-14 \le l \le 14$
Refl. measured	16691	8109
R_{int}	0.027	0.059
Param. refined	490	114
$R(F)/wR(F^2)$ (all reflexions)	0.0858 / 0.1166	0.0750 / 0.1394
$\Delta\rho_{fin}$ (max/min) [e Å^{-3}]	0.25 / −0.23	0.27 / −0.19

Results and Discussion

Bond distances, angles and torsion angles for **1** and **2** are listed in Tables 2 and 3, respectively. Views of the molecular structures of **1** and **2** are given in Figs. 1 and 2. Compound **1** crystallizes in the centrosymmetric space group $P\bar{1}$ with four crystallographically independent molecules in the unit cell. Each of these molecules has crystallographic inversion symmetry. They differ from each other in minor conformational details with regard to the torsion angles around the bonds adjacent to the central C–C bond and with regard to the orientation of the phenyl rings (Table 2). The conformational flexibility is most propably also the origin of the oc-

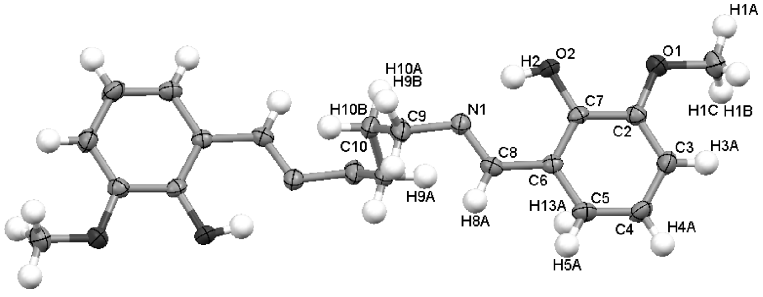

Fig. 1. The molecular structure of one of the four crystallographically independent, inversion-symmetric molecules of **1** in the crystal. Displacement ellipsoids are drawn at the 50 % probability level.

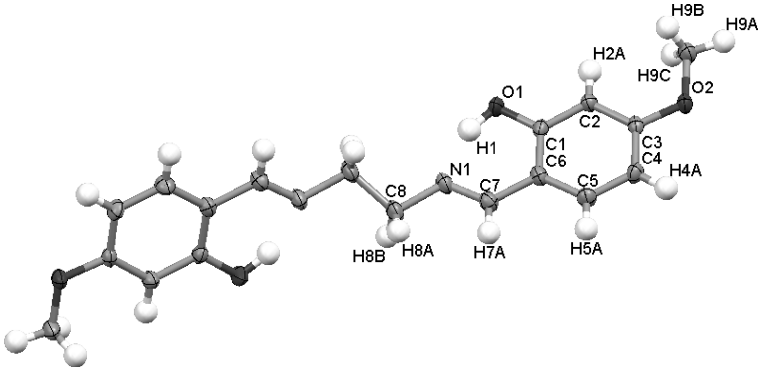

Fig. 2. The molecular structure of **2** having crystallographic C_2 symmetry. Displacement ellipsoids are drawn at the 50 % probability level.

Table 2. Selected bond lengths (Å), angles (deg), and torsion angles (deg) for **1** in the crystal. (For atomic numbering see Fig. 1).

Distances			
N(1)–C(9)	1.465(2)	C(9)–C(10)	1.521(3)
N(1)–C(8)	1.277(2)	C(7)–O(2)	1.352(2)
C(1)–O(1)	1.426(2)	C(2)–O(1)	1.372(2)
Angles			
C(8)–N(1)–C(9)	118.09(2)	N(1)–C(8)–C(6)	122.26(2)
N(1)–C(9)–C(10)	111.47(2)	C(6)–C(7)–O(2)	122.0(2)
C(9)–C(10)–C(10A)	112.90(2)	C(1)–O(1)–C(2)	117.25(2)
Torsion Angles			
C(6)–C(8)–N(1)–C(9)		−178.7	
C(16)–C(18)–N(2)–C(19)		−178.5	
C(26)–C(28)–N(3)–C(29)		179.9	
C(36)–C(38)–N(4)–C(39)		179.7	
C(8)–N(1)–C(9)–C(10)		110.4	
C(18)–N(2)–C(19)–C(20)		−114.8	
C(28)–N(3)–C(29)–C(30)		−107.1	
C(38)–N(4)–C(39)–C(40)		120.8	

currence of altogether four crystallographically independent molecules. Compound **2** has crystallographic C_2 symmetry.

Two types of intramolecular hydrogen bond (either N–H···O or N···H–O) can occur in Schiff bases [12]. The Schiff bases derived form salicylaldehyde always form the N···H–O type of hydrogen bonding regardless of the substituent at N (alkyl or aryl) [13]. In

Table 3. Selected bond lengths (Å), angles (deg), and torsion angles (deg) for **2** (primed atoms are related to those without a prime by a crystallographic two-fold axis). (For atomic numbering see Fig. 2).

Distances			
N(1)–C(7)	1.283(2)	C(9)–O(2)	1.438(2)
N(1)–C(8)	1.466(2)	C(7)–C(6)	1.453(2)
C(1)–O(1)	1.347(2)	C(3)–O(2)	1.372(2)
Angles			
C(8)–N(1)–C(7)	120.49(1)	C(9)–O(2)–C(3)	117.32(1)
N(1)–C(7)–C(6)	122.04(1)	C(6)–C(1)–O(1)	121.25(1)
Torsion Angles			
N(1)–C(8)–C(8)′–N(1)′		167.4(1)	
C(6)–C(7)–N(1)–C(8)		178.81(1)	
N(1)–C(7)–C(6)–C(1)		0.9(2)	

the title molecules, intramolecular hydrogen bonds occur between O(2) and N(1) (2.597(2) Å) and between O(4) and N(2) atoms (2.588(2) Å) for four independent molecules of **1** and between O(1) and N(1) atoms (2.587 (2) Å) for **2** (Tables 4 and 5). Clearly, the enolimine tautomer is favoured over the ketamine form. This is evident from the observed O(2)–C(7) bond lengths of 1.352(2) Å for **1** and O(1)–C(1) 1.347(2) Å for **2**, respectively, which are consistent with O–C single bonds; similarly the N(1)–C(8) distance of 1.277(2) Å for **1** and the N(1)–C(7) distance of 1.283(2) Å for **2** are consistent with N=C double bonding.

Table 4. Hydrogen bonds for the four crystallographically independent molecules of **1** (Å and deg).

D–H···A	D–H	H···A	D···A	D–H···A
O(2)–H(2) ···N(1)	0.90(2)	1.77(2)	2.597(2)	151(2)
O(4)–H(4) ···N(2)	0.85(2)	1.80(2)	2.588(2)	154(2)
O(6)–H(6) ···N(3)	0.97(2)	1.71(2)	2.596(2)	150(2)
O(8)–H(8) ···N(4)	0.97(2)	1.66(2)	2.566(2)	152(2)

Experimental Section

*Synthesis of compound **1***

To a solution of 174 mg (1.2 mmol) of 2-hydroxy-3-methoxybenzaldehyde in ethanol (10 mL) was added dropwise a solution of 52 mg (0.6 mmol) of 1,4-diaminobutane in ethanol (10 mL) and stirred at r. t. for 4 h. Immediately a yellow colour was observed and a precipitate started to form after 1 h. The yellow microcrystalline powder was collected by filtration. The solid was dissolved in a mixture of acetonitrile and methanol (1 : 1). After slow evaporation of the solvents, suitable crystals for XRD analysis were collected. M. p. 140 °C; yield 215 mg (95 %). – IR (KBr, cm^{-1}): ν = 1630 (C=N), 3433 (O–H), 1480, 1393, 1247, 1150, 1072 cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 13.50 (s, 1H, OH), 8.15 (s, 1H, CH=N), 6.97 (d, 2H), 6.59 (m, 1H), 3.67 (m, 3H), 3.47 (s, 2H), 1.64 (s, 2H). – MS (EI, 70 eV): *m/z* (%) = 356 (20) $[M]^+$, 205 (100) $[M–C_8H_8NO_2]^+$, 178 (60) $[M–C_{10}H_{12}NO_2]^+$.

*Synthesis of compound **2***

To a solution of 90 mg (0.6 mmol) of 2-hydroxy-4-methoxybenzaldehyde in ethanol (10 mL) was added dropwise a solution of 18 mg (0.3 mmol) of 1,2-diaminoethane in ethanol (10 mL) and stirred at r. t. for 4 h. The further procedure was the same as described for **1**. M. p. 166 °C; yield 104 mg (96 %). – IR (KBr, cm^{-1}): ν = 1622 (C=N), 3430 (O–H), 1431, 1382, 1275, 1210, 1155, 1107 cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 13.50 (s, 1H, OH), 8.02 (s, 1H, CH=N), 6.90 (d, 1H), 6.25 (s, 1H), 6.18 (d, 1H), 3.6 (m, 5H). – MS (EI, 70 eV): *m/z* (%) = 328 (4) $[M]^+$, 164 (100) $[M–C_9H_{10}NO_2]^+$, 133 (42) $[M–C_{11}H_{15}O]^+$.

Table 5. Hydrogen bond for **2** (Å and deg).

D–H···A	D–H	H···A	D···A	D–H···A
O(1)–H(1)···N(1)	0.95(3)	1.69(4)	2.587(2)	156(3)

Crystal structure determination

Crystals of **1** and **2** were mounted on an Bruker SMART 1K CCD diffractometer and a Nonius Kappa CCD diffractometer (MoK_α radiation, λ = 0.71073 Å), respectively. Crystal data, collection procedures and refinement results are summarized in Table 1 and selected bond lengths and angles are shown in Tables 2 and 3. The unit cell parameters were determined using SMART [14] and refined based on the positions of all strong reflections using SAINT [14]. Absorption correction was by SADABS [15] based on symmetry-equivalent and repeated reflections. The structure was solved by Direct Methods using SIR97 [16] and refined by full-matrix least-squares on F^2 using SHELXTL [17]. Molecular graphics were produced using DIAMOND-3 [18] and Mercury 1.4 [19]. Non-hydrogen atoms were refined anisotropically; hydrogen atoms were first located in a difference map and then refined.

CCDC 617156 (for **1**) and CCDC 622726 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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