

(E)-2-[(4-Chlorophenyl)iminomethyl]-5-methoxyphenol and (E)-2-[(2-chlorophenyl)iminomethyl]-5-methoxyphenol: X-ray and DFT-calculated structuresBaşak Koşar,^{a*} Çigdem Albayrak,^a Mustafa Odabaşoğlu^b and Orhan Büyükgüngör^c^aDepartment of Science Education, Sinop University, TR-57100 Sinop, Turkey,^bChemistry Program, Pamukkale University, 20159-Denizli, Turkey, and^cDepartment of Physics, Faculty of Arts and Sciences, Ondokuz Mayıs University, 55139 Samsun, Turkey

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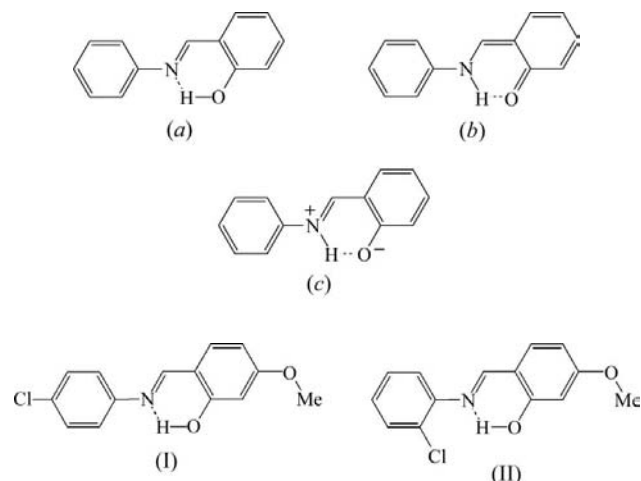
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The crystal structures of the title 4-chlorophenyl, (I), and 2-chlorophenyl, (II), compounds, both $C_{14}H_{12}ClNO_2$, have been determined using X-ray diffraction techniques and the molecular structures have also been optimized at the B3LYP/6-31 G(d,p) level using density functional theory (DFT). The X-ray study shows that the title compounds both have strong intramolecular $O-H \cdots N$ hydrogen bonds and that the crystal networks are primarily determined by weak $C-H \cdots \pi$ and van der Waals interactions. The strong intramolecular $O-H \cdots N$ hydrogen bond is evidence of the preference for the phenol-imine tautomeric form in the solid state. The IR spectra of the compounds were recorded experimentally and also calculated for comparison. The results from both the experiment and theoretical calculations are compared in this study.

Comment

Schiff bases are widely used as ligands in the field of coordination chemistry and are formed by reaction of a primary amine and an aldehyde (March, 1992). Schiff bases, especially *o*-hydroxy Schiff base derivatives, are members of one of the most commonly investigated classes of compound, and have attracted the interest of chemists and physicists because they show photochromism and thermochromism in the solid state. These photo- and thermochromic features are caused by proton transfer to the N atom from the O atom under the influence of light or temperature, respectively. It has been proposed that the molecules showing thermochromism are planar and that those showing photochromism are nonplanar (Moustakali-Mavridis *et al.*, 1980; Hadjoudis *et al.*, 1987).

o-Hydroxy Schiff bases exist either as phenol-imine (benzenoid) or keto-amine (quinoid) tautomers. Quinoid tautomers can also be found in the zwitterionic form and zwitterions can differ from keto-amines with respect to their N^+-H bond distances and the aromaticity of the rings. Depending on these tautomers, three different types of intramolecular hydrogen bonding are possible in *o*-hydroxy Schiff bases: (a) $O-H \cdots N$ in phenol-imine, (b) $N-H \cdots O$ in keto-amine and (c) ionic $N^+-H \cdots O^-$ in zwitterionic forms (see scheme).



These forms have been previously observed and investigated widely: for the phenol-imine form, see Ünver *et al.* (2002) and Karadayı *et al.* (2003); for the keto-amine form, see Pavlović & Sosa (2000) and Koşar *et al.* (2004); for the zwitterionic form, see Nazır *et al.* (2000) and Karabyık *et al.*

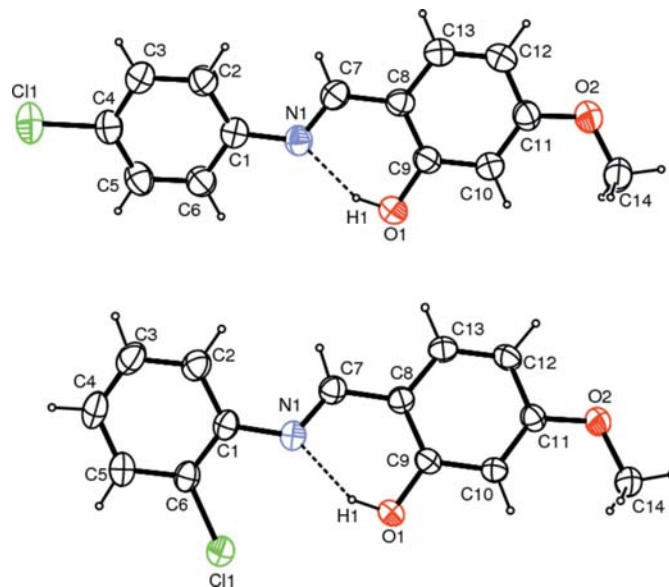


Figure 1
Views of the asymmetric units and the atom-numbering schemes for (I) (top) and (II) (bottom). Displacement ellipsoids are drawn at the 30% probability level and dashed lines indicate the intramolecular hydrogen bonds.

(2008). Related to this phenomenon, we present here the crystal and molecular structures of the title compounds, (I) and (II).

In computational procedures, the geometry optimization of the molecules leading to energy minima was achieved using the B3LYP hybrid exchange-correlation functional with the 6-31 G(d,p) basis set (Lee *et al.*, 1988; Becke, 1993). The calculations were started from the crystallographically achieved geometries of the molecules. All calculations in this work were carried out using the *GAUSSIAN03W* package (Frisch *et al.*, 2004). The optimized molecular geometries, total molecular energies, dipole moments, Mulliken charges and theoretical IR spectra were obtained from the computational process.

ORTEP-3 plots (Farrugia, 1997) showing the atom-numbering schemes of the title compounds are shown in Fig. 1. It is seen that the structures adopt phenol-imine tautomeric forms with C7=N1 double bonds and C9–O1 single bonds. These bond distances [1.282 (2) and 1.346 (2) Å for (I), and 1.279 (2) and 1.3451 (18) Å for (II)] are in good agreement with each other and with those observed for (*E*)-4-methoxy-2-[(4-nitrophenyl)iminomethyl]phenol [1.277 (2) and 1.351 (2) Å; Kõsar *et al.*, 2005] and *N*-(2-methyl-5-chlorophenyl)salicylalimine [1.281 (3) and 1.354 (3) Å; Dey *et al.*, 2001], which are also phenol-imine tautomers. On the other hand, in keto-amine tautomers of *o*-hydroxy Schiff bases, these distances show differences due to proton transfer. The same bond distances can be compared with the corresponding distances in 2-[[tris(hydroxymethyl)methyl]aminomethylene]cyclohexa-3,5-dien-1(2*H*)-one [1.3025 (16) and 1.2952 (18) Å] which is a keto-amine tautomer (Odabaşođlu *et al.*, 2003).

In the phenol-imine tautomeric form, both rings of the compound must be aromatic [see (*a*) in the scheme]. In order to provide further verification of the phenol-imine form in the solid state and investigate the aromaticity of the rings, HOMA (harmonic oscillator model of aromaticity) indices were calculated for compounds (I) and (II) (Krygowski, 1993). The HOMA index is equal to 1 for aromatic systems (like aromatic benzene) and 0 for non-aromatics. While the calculated indices of the chloro- and methoxy-substituted rings are 0.950 and 0.951, respectively, for (I), those of (II) are 0.967 and 0.939. These values also indicate that the compounds show

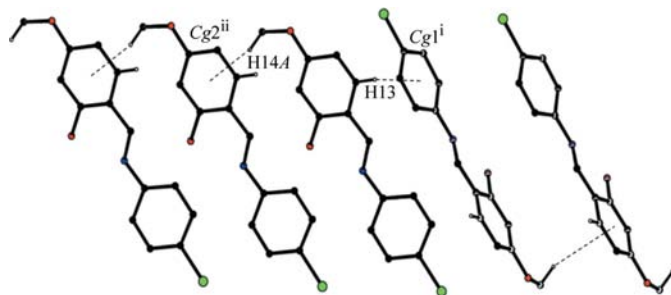


Figure 2
Part of the crystal structure of (I), showing the C–H··· π bonds. For clarity, H atoms not included in intermolecular bonding have been omitted. See Table 1 for symmetry codes.

phenol-imine tautomerism. In both molecules, the aromatic rings adopt an *E* configuration around the C=N double bonds and the dihedral angle between the two aromatic rings of the molecules is 15.39 (2)° for (I) and 24.49 (8)° for (II). Against this background, we can say that the compounds are non-planar and display photochromic features. On the whole, there is harmony between the X-ray crystallographic results of both title compounds.

The title compounds display strong intramolecular hydrogen bonds between atoms O1 and N1, which is a common feature of *o*-hydroxysalicylidene systems (Yildiz *et al.*, 1998; Filarowski *et al.*, 2003). The crystal structures are stabilized by weak van der Waals and C–H··· π interactions. Figs. 2 and 3 illustrate these C–H··· π interactions. The geometric parameters of the intramolecular hydrogen bonds and the intermolecular C–H··· π interactions are listed in Tables 1 and 2.

In DFT/B3LYP calculations, the total energy of the optimized geometry and the dipole moment of the molecules are obtained as -5.2583×10^{-15} J and 2.9778 D for (I) and -5.2583×10^{-15} J and 2.3162 D for (II). It is not surprising that the molecules have the same total energy according to DFT/B3LYP calculations because their only difference is the position of the Cl atom. Mulliken charges were calculated by determining the electron population of each atom as defined by the basis sets. According to the calculated results for Mulliken atomic charge analysis, atoms N1, O1 and O2 have larger negative charges relative to other atoms for both molecules, as expected (Table 3).

Selected bond distances, angles and torsion angles from the X-ray crystallographic and computational results for (I) and (II) are compared in Table 3. There are no significant differences between the experimental and DFT/B3LYP calculated geometric parameters, except for the torsion angles. For example, the maximum deviations between the experimental and calculated parameters is about 0.024 Å for bond lengths, about 0.43° for bond angles and about 14.22° for torsion angles. DFT and similar calculations are known to underestimate interactions such as inter- and intramolecular

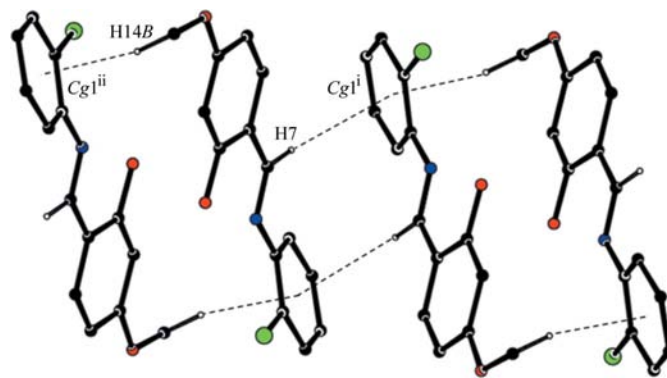


Figure 3
Part of the crystal structure of (II), showing the C–H··· π bonds. See Table 2 for symmetry codes.

hydrogen bonds because they consider molecules in the gaseous phase (*in vacuo*).

The experimental and computational IR spectra of compounds (I) and (II) are compared in Table 5. The DFT-based IR results show significant differences from experimental values for C=N, O—H and C—O stretching due to the intramolecular hydrogen bond between N and O for both molecules. In experimental-based IR results, while C=N stretching is shifted to lower frequency, O—H stretching is widened to the 2000–3000 cm⁻¹ range.

Experimental

Compound (I) was prepared by refluxing for 1 h under stirring a mixture of a solution of 4-methoxysalicylaldehyde (0.5 g, 3.3 mmol) in ethanol (20 ml) and a solution of 4-chloroaniline (0.42 g, 3.3 mmol) in ethanol (20 ml). Crystals of (I) suitable for X-ray analysis were obtained from ethanol by slow evaporation (yield 80%, m.p. 396–397 K). Compound (II) was prepared by refluxing for 1 h under stirring a mixture of a solution of 4-methoxysalicylaldehyde (0.5 g, 3.3 mmol) in ethanol (20 ml) and a solution of 2-chloroaniline (0.42 g, 3.3 mmol) in ethanol (20 ml). Crystals of (II) suitable for X-ray analysis were obtained from ethanol by slow evaporation (yield 73%, m.p. 386–387 K). The IR spectra of the title compounds were recorded on a KBr disc with a Bruker 2000 FT IR spectrometer.

Compound (I)

Crystal data

C ₁₄ H ₁₂ ClNO ₂	<i>V</i> = 1265.2 (2) Å ³
<i>M_r</i> = 261.70	<i>Z</i> = 4
Monoclinic, <i>P</i> 2 ₁ / <i>c</i>	Mo <i>K</i> α radiation
<i>a</i> = 5.5859 (6) Å	<i>μ</i> = 0.29 mm ⁻¹
<i>b</i> = 8.9617 (6) Å	<i>T</i> = 293 K
<i>c</i> = 25.333 (3) Å	0.52 × 0.31 × 0.12 mm
<i>β</i> = 93.880 (9)°	

Data collection

Stoe IPDS2 diffractometer	10988 measured reflections
Absorption correction: integration (<i>X-RED</i> ; Stoe & Cie, 2002)	2440 independent reflections
<i>T</i> _{min} = 0.864, <i>T</i> _{max} = 0.968	1505 reflections with <i>I</i> > 2σ(<i>I</i>)
	<i>R</i> _{int} = 0.036

Refinement

<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.038	H atoms treated by a mixture of independent and constrained refinement
<i>wR</i> (<i>F</i> ²) = 0.098	<i>Δρ</i> _{max} = 0.11 e Å ⁻³
<i>S</i> = 0.98	<i>Δρ</i> _{min} = -0.17 e Å ⁻³
2440 reflections	
167 parameters	
1 restraint	

Table 1

Hydrogen-bond geometry (Å, °) for (I).

*Cg*₁ is the centroid of the chlorophenyl ring and *Cg*₂ is the centroid of the methoxyphenyl ring.

<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>
O1—H1...N1	0.851 (16)	1.806 (18)	2.596 (2)	154 (2)
C13—H13... <i>Cg</i> ₁ ⁱ	0.93	3.04	3.896 (2)	154
C14—H14A... <i>Cg</i> ₂ ⁱⁱ	0.96	3.10	3.975 (2)	153

Symmetry codes: (i) $-x + 2, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $x - 1, y, z$.

Table 2

Hydrogen-bond geometry (Å, °) for (II).

*Cg*₁ is the centroid of the chlorophenyl ring.

<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>
O1—H1...N1	0.85 (2)	1.82 (2)	2.5991 (18)	150 (2)
C7—H7... <i>Cg</i> ₁ ⁱ	0.96 (2)	2.98 (2)	3.893 (2)	160.2 (17)
C14—H14B... <i>Cg</i> ₁ ⁱⁱ	1.01 (2)	2.91 (2)	3.864 (3)	156.9 (17)

Symmetry codes: (i) $-x + 1, y, -z + \frac{1}{2}$; (ii) $-x + 1, -y, -z$.

Table 3

Mulliken atomic charges for (I) and (II) (e).

Atom	(I)	(II)
Cl1	-0.024	-0.005
N1	-0.609	-0.605
O1	-0.569	-0.566
O2	-0.512	-0.513
C1	0.266	0.292
C2	-0.095	-0.093
C3	-0.085	-0.099
C4	-0.093	-0.079
C5	-0.079	-0.082
C6	-0.092	-0.128
C7	0.170	0.171
C8	0.040	0.039
C9	0.305	0.307
C10	-0.164	-0.164
C11	0.361	0.361
C12	-0.126	-0.126
C13	-0.137	-0.136
C14	-0.083	0.083
H1	0.354	0.366

Table 4

Comparison of the optimized and experimental geometric parameters of (I) and (II) (Å, °).

	(I)		(II)	
	X-ray	DFT/B3LYP	X-ray	DFT/B3LYP
Cl1—C4	1.7404 (19)	1.758	1.7309 (18)†	1.755†
C1—N1	1.410 (2)	1.404	1.4097 (19)	1.398
N1=C7	1.282 (2)	1.297	1.279 (2)	1.296
C7—C8	1.436 (2)	1.440	1.439 (2)	1.439
C9—O1	1.346 (2)	1.337	1.3451 (18)	1.336
C11—O2	1.359 (2)	1.357	1.3567 (18)	1.357
C1—N1=C7	121.88 (17)	121.34	120.76 (15)	121.17
N1=C7—C8	122.02 (18)	122.38	121.89 (16)	122.24
C6—C1—N1=C7	162.47 (17)	148.23	154.24 (16)	145.48
C1—N1=C7—C8	-177.86 (16)	-177.15	-177.44 (15)	-176.61
N1=C7—C8—C13	-178.25 (18)	-179.26	-179.85 (17)	-179.85

† Cl1—C6.

Table 5

Comparison of the observed and calculated vibrational spectra of (I) and (II).

	(I)		(II)	
	Experimental (cm ⁻¹)	DFT/B3LYP (cm ⁻¹)	Experimental (cm ⁻¹)	DFT/B3LYP (cm ⁻¹)
<i>ν</i> (C—Cl)†	1089	1108	1112	1060
<i>ν</i> (N=C)†	1611	1673	1612	1674
N=C—H‡	1397	1393	1394	1392
<i>ν</i> (C—C)†	1564	1561	1562	1560
<i>ν</i> (C—C)†	1442	1447	1471	1477
<i>ν</i> (O—H)†	2000–3000	3121	2000–3000	3157

† Stretching. ‡ Bending.

Compound (II)

Crystal data

$C_{14}H_{12}ClNO_2$	$V = 2489.3 (5) \text{ \AA}^3$
$M_r = 261.70$	$Z = 8$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 22.446 (3) \text{ \AA}$	$\mu = 0.30 \text{ mm}^{-1}$
$b = 7.2259 (7) \text{ \AA}$	$T = 293 \text{ K}$
$c = 16.727 (2) \text{ \AA}$	$0.50 \times 0.47 \times 0.21 \text{ mm}$
$\beta = 113.428 (9)^\circ$	

Data collection

Stoe IPDS2 diffractometer	10001 measured reflections
Absorption correction: integration (<i>X-RED</i> ; Stoe & Cie, 2002)	2885 independent reflections
$T_{\min} = 0.838$, $T_{\max} = 0.939$	1854 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.039$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$	211 parameters
$wR(F^2) = 0.102$	All H-atom parameters refined
$S = 0.91$	$\Delta\rho_{\max} = 0.14 \text{ e \AA}^{-3}$
2885 reflections	$\Delta\rho_{\min} = -0.24 \text{ e \AA}^{-3}$

In (I), all H atoms except for H1 were refined using a riding model, with C—H distances of 0.96 Å for the methyl group and 0.93 Å for aromatic groups, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The hydroxy H atom was located in a difference Fourier map and its position and isotropic displacement parameter were refined while applying an O—H distance restraint of 0.82 (2) Å. All H atoms in (II) were located in a difference Fourier map in the latter stage of the refinement procedure and their positions and isotropic displacement parameters were refined freely.

For both compounds, data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009) and *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *enCIFer* (Allen *et al.*, 2004).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3113). Services for accessing these data are described at the back of the journal.

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