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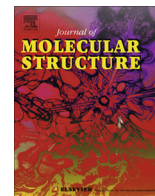
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# Synthesis, characterization, crystal structure determination and computational study of the two new bidentate O, N Schiff bases derived from bromosalicylaldehyde and amines containing alkyl halide pendant groups

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## H I G H L I G H T S

- Two new Schiff base compounds have been synthesized.
- They were characterized by CHN and X-ray analysis, FT-IR and <sup>1</sup>H NMR spectroscopy.
- Quantum theory of atoms in molecules has been used to find intramolecular interactions.
- There is a strong hydrogen bonding between nitrogen of imine and oxygen of phenol.
- They are partially covalent and partially electrostatic in nature.

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## A B S T R A C T

Two new Schiff base compounds 2-[(E)-[2-(bromoethyl)imino]methyl]-4-bromophenol (**1**) and 2-[(E)-[2-(chloroethyl)imino]methyl]-4-bromophenol (**2**) have been synthesized and characterized by FT-IR and <sup>1</sup>H NMR spectroscopy, elemental analysis, thermal studies and single-crystal X-ray diffraction. They crystallize in the triclinic system, space group *P*-1. Both Schiff base compounds **1** and **2** display a *trans* configuration with respect to the C=N double bond. Quantum theory of atoms in molecules (QTAIM) has been also used to find intramolecular interactions and investigate their chemical nature. The results show that in both of the compounds **1** and **2**, there is a hydrogen bonding between nitrogen of imine and oxygen of phenol which is considerably stronger than normal hydrogen bonds. In addition, it has been shown that these hydrogen bonds are partially covalent and partially electrostatic in nature, in contrast to normal hydrogen bonds, which are usually considered as electrostatic interactions.

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## 1. Introduction

Azomethines (known as Schiff-bases), having imine groups (—C=N—), are formed by the condensation reaction of primary amines with aldehydes or ketones. They are some of the most widely used organic compounds in different aspects. They played central role in development of coordination chemistry of transition metals [1,2]. These compounds used for industrial purposes such

as pigments, catalysts, intermediates in organic synthesis and as polymer stabilizers [3]. Schiff bases are an important class of compounds in both the medicinal and pharmaceutical fields [4–6] and have also found to exhibit a broad range of biological activities, including antifungal, antibacterial, antimalarial, antiproliferative, anti-inflammatory, antiviral, and antipyretic properties [7,8]. In the area of bioinorganic chemistry interest in Schiff bases complexes with transition and inner-transition metals has centered on the role of such complexes in providing synthetic interesting models for the metal-containing sites in metallo-proteins and -enzymes [7,9–16].

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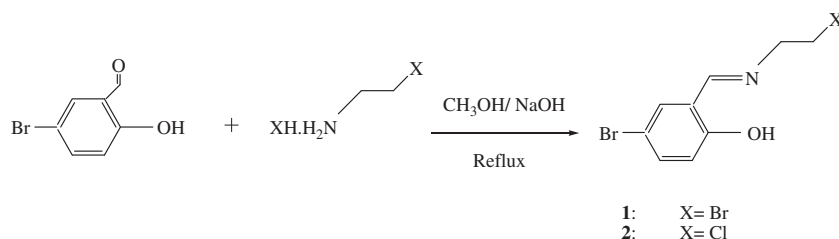
Scheme 1. Preparation procedures of Schiff base compounds **1** and **2**.

Table 1

Crystal data and summary of experimental details.

	1	2
Empirical formula	C <sub>9</sub> H <sub>9</sub> Br <sub>2</sub> NO	C <sub>9</sub> H <sub>9</sub> BrClNO
Formula weight	306.99	262.53
Crystal system	Triclinic	Triclinic
Space group	P	P
T (K)	296 (2)	296 (2)
a (Å)	4.6637 (3)	4.6065 (2)
b (Å)	9.0052 (5)	8.8898 (5)
c (Å)	12.5622 (7)	12.4802 (7)
α (deg)	84.600 (2)	84.992 (3)
β (deg)	83.333 (2)	83.703 (2)
γ (deg)	89.713 (2)	88.848 (3)
V (Å <sup>3</sup> )	521.68 (5)	506.02 (5)
Z	2	2
F <sub>000</sub>	296	260
D <sub>x</sub> (Mg m <sup>-3</sup> )	1.954	1.723
μ (mm <sup>-1</sup> )	7.73	4.28
θ <sub>min</sub> , θ <sub>max</sub>	2.9, 26.0	2.3, 25.7
T <sub>min</sub> , T <sub>max</sub>	0.524, 0.745	0.564, 0.745
Measured reflections	4649	3471
Independent reflections	2021	1901
Reflection with I > 2σ(I)	1717	1561
R <sub>int</sub>	0.016	0.014
S	1.00	0.96
R[F <sup>2</sup> > 2σ(F <sup>2</sup> )]	0.027	0.027
wR(F <sup>2</sup> )	0.066	0.079
Parameters	119	119
Δρ <sub>max</sub> , Δρ <sub>min</sub> (eÅ <sup>-3</sup> )	0.39, -0.58	0.47, -0.21
Index range	-5 ≤ h ≤ 5 -10 ≤ k ≤ 11 -15 ≤ l ≤ 15	-5 ≤ h ≤ 5 -10 ≤ k ≤ 6 -15 ≤ l ≤ 15

We started to investigate the synthesis, characterization, crystal structure determination of some new bidentate (O,N) Schiff bases ligands derived from substituted salicylaldehydes and metal amines containing alkyl halide pendant groups and their metal complexes [17,18]. In this research we describe the synthesis, characterization, crystal structure determination and computational study of 2-[(E)-[2-(bromoethyl)imino]methyl]-4-bromo (**1**) and 2-[(E)-[2-(chloroethyl)imino]methyl]-4-bromo (**2**) and Schiff base compounds (Scheme 1). In order to gain a deeper understanding of the nature of intramolecular interactions, a theoretical study has been also carried out. Attention was focused on the electron density and it is Laplacian, kinetic energy density, potential energy density and energy density from Bader's quantum theory of atoms in molecules (QTAIM) [19].

## 2. Experimental

### 2.1. Physical techniques and materials

All reagents and solvents for synthesis and analysis were commercially available and used as received without further purifications. Infrared spectra were recorded using KBr disks on a FT-IR

Table 2

Selected and calculated bond distances (Å), angles (°) and torsion angles (°).

	1	1*	2	2*
Br(2)–C(1)	1.954(3)	1.974	–	–
Cl(1)–C(1)	–	–	1.797(3)	1.813
Br(1)–C(6)	1.904(3)	1.917	1.902(2)	1.917
O(1)–C(9)	1.352(3)	1.340	1.345(3)	1.340
N(1)–C(3)	1.270(3)	1.281	1.264(3)	1.281
N(1)–C(2)	1.457(3)	1.454	1.449(3)	1.453
C(2)–C(1)	1.500(4)	1.529	1.499(4)	1.524
C(3)–N(1)–C(2)	119.4(2)	119.2	119.5(2)	119.2
C(5)–C(6)–Br(1)	119.9(2)	119.9	119.55(18)	119.9
C(7)–C(6)–Br(1)	119.2(2)	119.6	119.16(17)	119.6
N(1)–C(3)–C(4)	121.0(2)	122.6	121.9(2)	122.6
N(1)–C(2)–C(1)	111.0(2)	109.0	111.1(2)	109.2
C(2)–C(1)–Br(2)	111.5(2)	110.7	111.16(18)	110.5
O(1)–C(9)–C(8)	118.8(2)	118.7	118.6(2)	118.7
H(1)–O(1)–C(9)–C(8)	–178.4(2)	179.67	–177.7(2)	179.66
C(2)–N(1)–C(3)–C(4)	179.5(2)	179.94	180.0(2)	179.79
C(2)–N(1)–C(3)–H(3)	–0.5(4)	0.28	0.0(4)	0.15
C(3)–N(1)–C(2)–H(1)	118.8(3)	122.19	–118.5(2)	123.51
C(8)–C(7)–C(6)–C(5)	0.4(4)	–0.02	–0.1(4)	–0.2
Br(1)–C(6)–C(5)–C(4)	179.6(2)	179.96	–179.7(2)	179.99
N(1)–C(3)–C(4)–C(5)	177.4(3)	179.90	–177.1(2)	179.96
N(1)–C(3)–C(4)–C(9)	–3.6(4)	–0.08	4.3(4)	–0.03
C(5)–C(4)–C(9)–O(1)	–179.2(2)	179.96	178.9(2)	179.96
C(7)–C(8)–C(9)–O(1)	179.1(3)	179.97	–178.7(2)	179.98
Br(2)–C(1)–C(2)–N(1)	–74.6(2)	177.11	–	–
Cl(1)–C(1)–C(2)–N(1)	–	–	72.9(2)	177.46

\* Calculated values.

Perkin–Elmer spectrophotometer. Elemental analyses were carried out using a Heraeus CHN–O–Rapid analyzer. <sup>1</sup>H NMR spectra were measured on a BRUKER DRX-500 AVANCE spectrometer at 500 MHz. All chemical shifts are reported in δ units downfield from TMS.

### 2.2. Preparation of the 2-[(E)-[2-(bromoethyl)imino]methyl]-4-bromophenol (**1**)

To a 250 ml round bottom flask containing 150 ml absolute methanol were added 10 mmol of 4-bromo-2-hydroxy benzaldehyde, 10 mmol of 2-bromoethyl ammonium hydrobromide and 10 mmol of NaOH and the content was refluxed with stirring for 4 h. After evaporating the solvent, the yellow precipitate was collected and washed with slightly cooled water and then with 1:1 mixture of n-hexane and dichloromethane. Yield: 2.24 g (73%). The yellow crystals were obtained by the crystallization of precipitate in 1:1 mixture of chloroform and methanol. *Anal.* Calc. for C<sub>9</sub>H<sub>9</sub>Br<sub>2</sub>NO: C, 35.35; H, 2.75; N, 4.55%. Found: C, 35.18; H, 2.93; N, 4.56%. IR (KBr pellet, cm<sup>-1</sup>): 3350–3480 (b, O–H, phenolic), 2840–3050 (w, C–H aliphatic and aromatic), 1636 (s, C=N), 1436, 1481, 1581, 1602 (m, C=C), 1269 (m, C–O). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ (ppm)): 13.00 (s, 1H: –O–H), 8.29 (s, 1H: H–C=N–), 7.4 (d, 1H: Ar–H:), 7.3 (d, 1H: Ar–H:), 6.8 (s, 1H: Ar–H:), 4.01 (t, 2H: –CH<sub>2</sub>Br) and 3.65 (t, 2H: –N–CH<sub>2</sub>–).

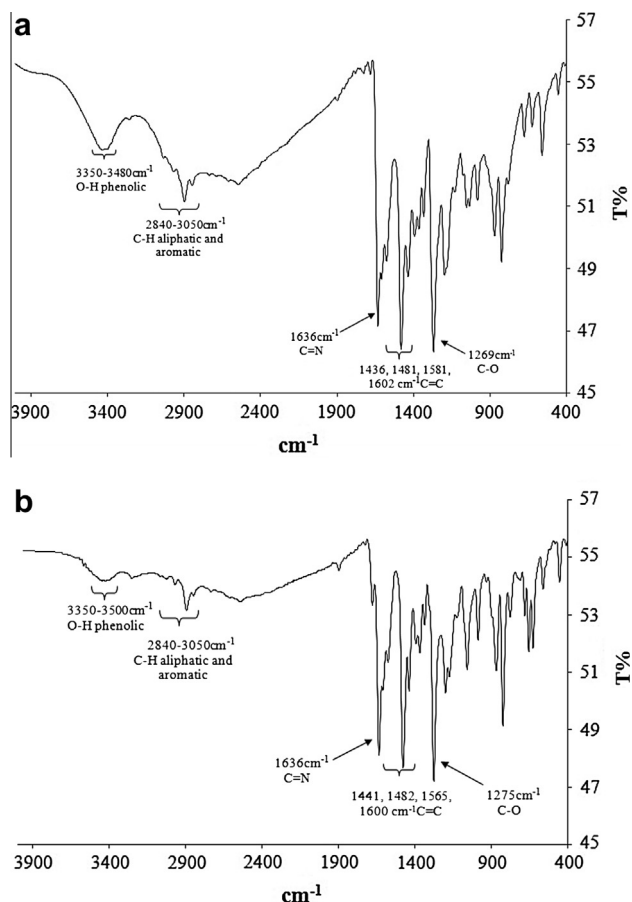


Fig. 1. FT-IR spectrum of 1(a) and 2(b).

### 2.3. Preparation of the 2-((E)-[2-(chloroethyl)imino]methyl)-4-bromophenol (2)

The Schiff base compound (2) was prepared in similar to the preparation of the Schiff base compound (1) except 2-chloroethyl ammonium hydrochloride was used instead of 2-bromoethyl

ammonium hydrobromide. Yield: 2.15 g (82%). The yellow crystals were obtained by the crystallization of precipitate in 1:1 mixture of chloroform and methanol. *Anal.* Calc. for C<sub>9</sub>H<sub>9</sub>BrClNO: C, 41.21; H, 3.31; N, 5.34%. Found: C, 41.13; H, 3.42; N, 5.34%. IR (KBr pellet, cm<sup>-1</sup>): 3350–3500 (b, O–H, phenolic), 2840–3050 (w, C–H aliphatic and aromatic), 1636 (s, C=N), 1441, 1482, 1565, 1600 (m, C=C), 1275 (m, C–O). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ (ppm)): 13.02 (s, 1H: –O–H), 8.31 (s, 1H: H–C=N–), 7.42 (d, 1H: Ar–H:), 7.40 (d, 1H: Ar–H:), 6.80 (s, 1H: Ar–H:), 3.93 (t, 2H: –CH<sub>2</sub>Cl) and 3.81 (t, 2H: –N–CH<sub>2</sub>–).

### 2.4. X-ray structure determination

A Single crystal of the dimension 0.49 mm × 0.15 mm × 0.10 mm of 1 and 0.43 mm × 0.39 mm × 0.10 mm of 2 were chosen for X-ray diffraction study. Diffraction data were measured on a Bruker–Nonius X8 ApexII diffractometer equipped with a CCD area detector by using graphite-monochromated Mo Kα radiation ( $k = 0.71073 \text{ \AA}$ ) generated from a sealed tube source. Data were collected and reduced by smart and saint software [20] in the Bruker package. The structures were solved by direct methods [21] and then developed by least squares refinement on  $F^2$  [22,23]. All non-H atoms were placed in calculated positions and refined as isotropic with the “riding-model technique”. Crystallographic data and details of the data collection and structure solution and refinements are listed in Table 1. Bond distances, angles and torsion angles are listed in Table 2.

## 3. Results and discussion

### 3.1. Synthesis and characterization

By reaction of eqimolar of 4-bromo-2-hydroxybenzaldehyde with 2-bromoethyl ammonium hydrobromide and 2-chloroethyl ammonium hydrochloride in methanol in reflux conditions in two separated reactions the titled compounds 1 and 2 were prepared (Scheme 1). They were characterized by the elemental and X-ray analysis, FT-IR and <sup>1</sup>H NMR spectra. The chemical composition of the Schiff base compounds 1 and 2 were determined by elemental (CHN) analysis. The results of this analysis agree finely with calculated amounts that confirm the chemical compositions of them. The chemical structures of the Schiff bases of 1 and 2 were

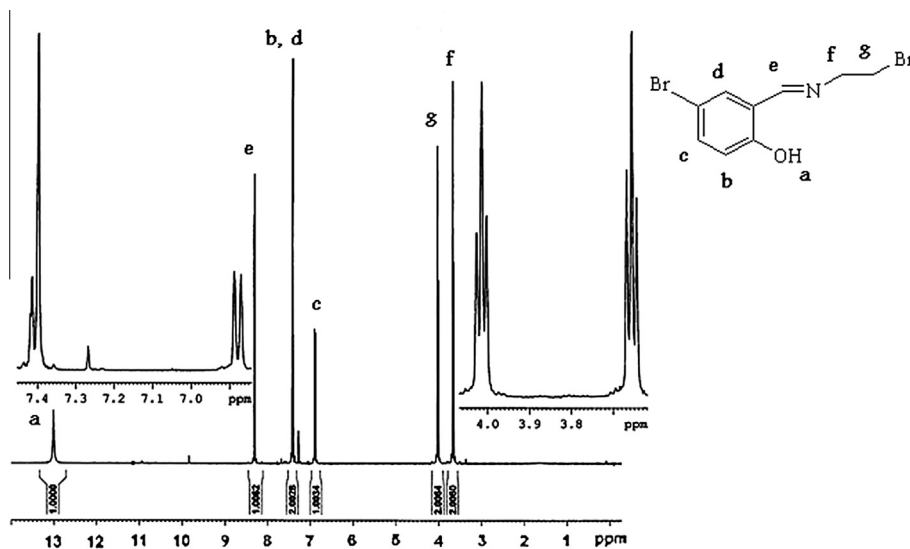


Fig. 2. <sup>1</sup>H NMR spectrum of 1.

determined by FT-IR and  $^1\text{H}$  NMR spectra and approved with crystal structure determination by X-ray analysis.

### 3.2. FT-IR spectrum

The characteristic band in the FT-IR spectra of **1** and **2** is the appearance of the strong band at  $1636\text{ cm}^{-1}$ , attributed to the  $\text{—C=N—}$  stretching vibration frequencies. The FT-IR spectrum of **1** and **2** also show several weak bands for the aromatic and aliphatic C—H stretching vibration frequencies in the region  $2800\text{--}3050\text{ cm}^{-1}$ , and strong bands for the aromatic C=C stretching

bonds in the region  $1300\text{--}1500\text{ cm}^{-1}$  [24,25]. Fig. 1 shows the FT-IR spectra of **1** and **2**.

### 3.3. $^1\text{H}$ NMR spectrum

The Schiff base compounds **1** and **2** have 7 kinds of protons. All of these kinds of protons show a distinct signal in  $^1\text{H}$  NMR spectrum of **1** and **2**. In the down field region of each spectrum, one singlet peak is appeared at 13.00 and 13.02 ppm attributed to the phenolic protons of Schiff base compounds **1** and **2**, respectively. These peaks were much shifted to the higher chemical shifts

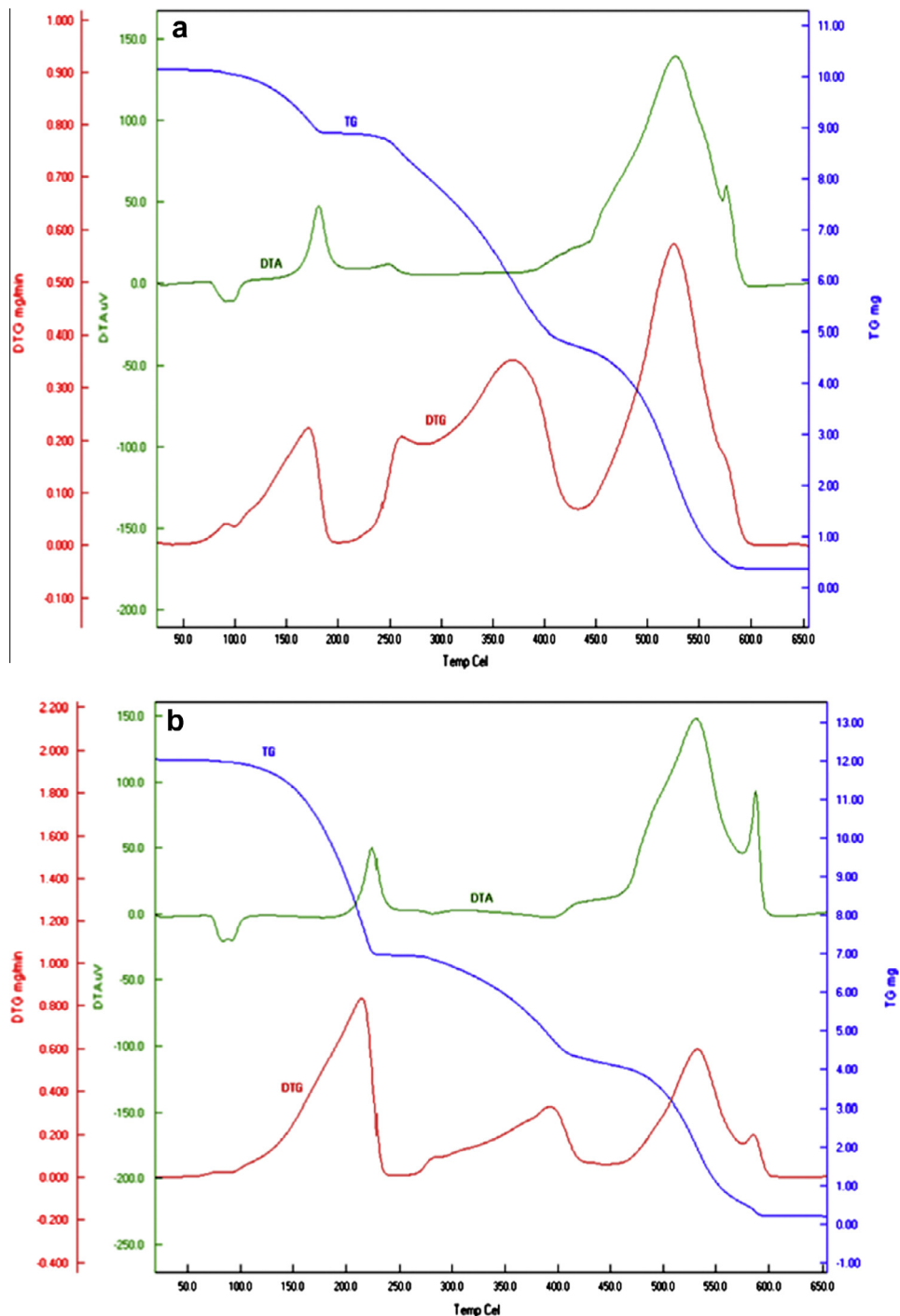


Fig. 3. The TGA/DTG/DTA profiles of the compounds **1**(a) and **2**(b).

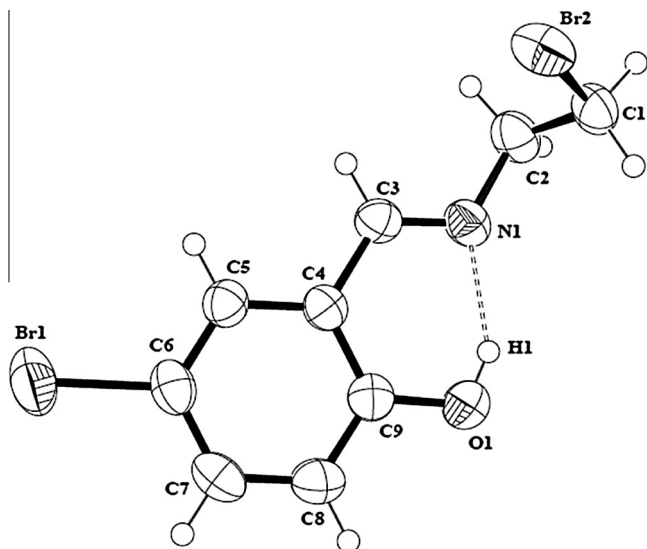


Fig. 4. An ORTEP view of **1**, showing 50% probability displacement ellipsoids.

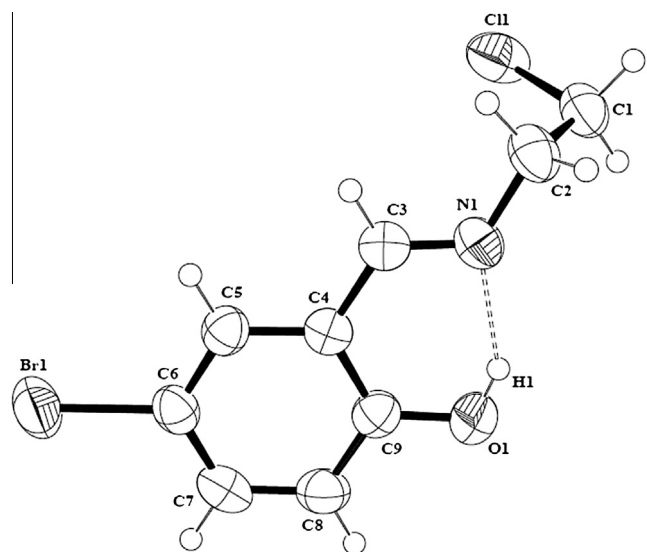


Fig. 5. An ORTEP view of **2**, showing 50% probability displacement ellipsoids.

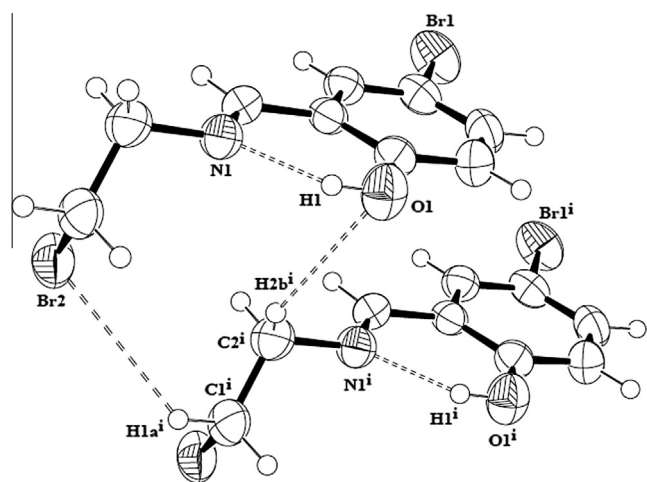


Fig. 6. Packing diagram of **1**.

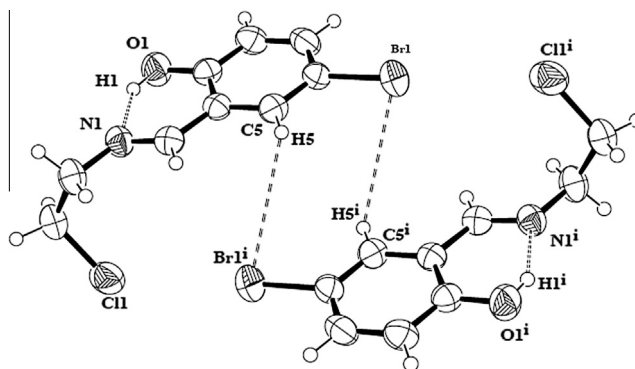


Fig. 7. Packing diagram of **2**.

because of the formation of strong intramolecular hydrogen bonding between the phenolic protons and nitrogen of imines. Another singlet peaks are seen about 8.3 ppm for each Schiff base compounds that corresponded to the protons of imines ( $\text{H}-\text{C}=\text{N}-$ ) in these Schiff bases. The protons of aromatic ring are appeared in the region of 6.8–7.5 ppm as two distinct doublet and one singlet. Each two sets of protons of  $-\text{N}-\text{CH}_2-$  and  $-\text{CH}_2\text{Cl}$  or  $-\text{CH}_2\text{Br}$  are showed a triplet peak in 3.6–4–1 ppm, for Schiff base compounds **1** and **2**. Fig. 2 shows the  $^1\text{H}$  NMR spectrum of the **1**.

#### 3.4. Thermal studies

The TGA/DTG/DTA profiles of the two compounds **1** and **2** are given in Fig. 3. Because of existing the different functional groups on the two compounds **1** and **2**, they are decomposed in four stages about the range of 90–600 °C but the thermal decomposition trends of them are not the same.

#### 3.5. Description of the crystal structures

The title compounds **1** and **2** crystallize in the triclinic space group *P*. The molecular structure of **1** and **2** with the atom numbering scheme is given in Figs. 4 and 5, respectively. All bonds distances and angles are normal and are in good agreement with those reported in similar Schiff-base compounds [24,25]. The  $\text{C3}=\text{N1}$  bond length of 1.270(3) Å in **1**, and 1.265(3) Å in **2** conform to the value for a double bond, while the  $\text{C2}-\text{N1}$  bond length of 1.4557(3) Å in **1**, and 1.447(3) Å in **2** conform to the value for a single bond, like in similar Schiff-base compounds [21,22]. The bond angle  $\text{C4}-\text{C3}-\text{N1}$  is 121.0(2)° and 121.9(2)°, respectively in **1** and **2**, which is consistent with the  $sp^2$  hybrid character of C3 atom, while the bond angle  $\text{C3}-\text{N1}-\text{C2}$  is 119.3(2)° and 119.5(2)°, respectively in **1** and **2**, which is consistent with the  $sp^2$  hybrid character of N1 atom.

Ortho position to the imine group of Schiff-base occupied with the OH is interesting due to the existence of  $\text{O}-\text{H}\cdots\text{N}$  hydrogen bond and possibility of tautomerism between enol-imine and keto-amine form in 2-hydroxy Schiff bases [26,27]. In the structures of Schiff base **1** and **2**, there is an intramolecular  $\text{O1}-\text{H1}\cdots\text{N1}$  hydrogen bond (Figs. 6 and 7 and Table 3) as in the Schiff bases derived from salicylaldehyde that always form the  $\text{O}-\text{H}\cdots\text{N}$  type of hydrogen bonding, regardless of the nature of the N substituent [28,29]. Molecular packing of **1** and **2** can be viewed molecules held together by various intermolecular hydrogen bonds (Figs. 6 and 7 and Table 3).

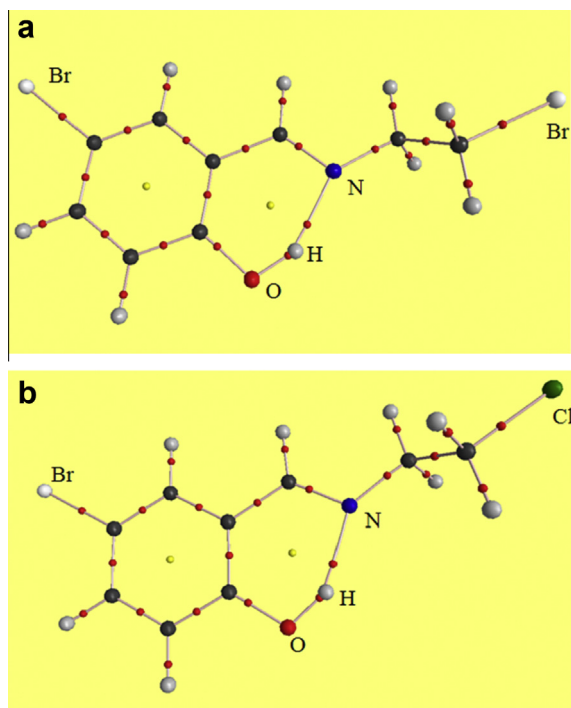
#### 3.6. Theoretical studies

It is well known that the quantum theory of atoms in molecules (QTAIM) provides a powerful tool for characterizing the chemical



**Table 3**  
Hydrogen bonds of 1 and 2.

Molecule	Interaction	D—H...A	D—H	H...A	D...A	D—H...A
1	Intramolecular	O1—H1...N1	0.820	1.845	2.575	147.681
	Intermolecular	C2—H2b...O1	0.969	2.818	3.612	139.647
	Intermolecular	C1—H1a...Br2	0.970	3.127	3.803	128.169
2	Intramolecular	O1—H1...N1	0.820	1.851	2.580	147.344
	Intermolecular	C5—H5...Br1	0.930	3.488	4.039	120.430

**Fig. 8.** Molecular graphs of 1(a) and 2(b), red points indicate the bond critical points (BCPs) between bonded atoms.**Table 4**  
QTAIM parameters (in a.u.) at the BCP of intramolecular N...H hydrogen bonds.

Molecule	$\rho_b$	$\nabla^2\rho_b$	$G_b$	$V_b$	$H_b$
1	0.048	0.111	0.036	−0.044	−0.008
2	0.048	0.111	0.036	−0.044	−0.008

**Table 5**  
Theoretical geometries of intramolecular hydrogen bonds (Bond distances are in Angstrom and angles are in degree).

	D—H...A	D—H	H...A	D...A	D—H...A
1	O—H...N	0.993	1.750	2.638	147.066
2	O—H...N	0.993	1.749	2.637	147.069

bonds [30,31]. This theory uses the electron density as an information source to describe atoms, bonds and molecules. So, to obtain the electron densities, Gaussian 03 program [32] has been used to generate electronic wavefunctions. To investigate intramolecular interactions, molecular geometries have optimized at B3LYP/6-311++G(d, p). Geometrical parameters (bond lengths, angles and dihedrals) of the studied compounds have been listed in Table 2. QTAIM calculations have carried out with AIMAll suite of programs [33]. In this part of article, we will use terminology of QTAIM, which has been reviewed elsewhere [30,31].

In QTAIM viewpoint, a chemical bond (including covalent, ionic, van der Waals, hydrogen bond, etc.) is always accompanied with a bond path (BP) and a bond critical point (BCP) between the bonded atoms. The molecular graphs (the set of BPs and BCPs) of the single molecules of this work have been shown in Fig. 8. As indicated, in addition to usual bonds, the molecular graphs indicate a BP and a BCP between nitrogen and hydrogen, which confirms that there is an intramolecular hydrogen bond (H-bond) in these molecules. Interestingly, each BCP contains a wealth of chemical information that properly describes the nature of the corresponding chemical bond. The values of electron density,  $\rho_b$ , Laplacian of electron density,  $\nabla^2\rho_b$ , kinetic energy density,  $G_b$ , potential energy density,  $V_b$ , and electronic energy density,  $H_b$ , at the BCP are the parameters that are usually used to characterize a chemical bond. Normal H-bonds are characterized as electrostatic interaction; a  $\rho_b$  value at the BCP, which lies within the range 0.002, 0.04 a.u., and positive values for  $\nabla^2\rho_b$  and  $H_b$  at the BCP [2]. These values for the BCP of the H-bonds in the compounds of the current work have been listed in Table 4. The values of  $\rho_b$  of these compounds are slightly larger than that of normal hydrogen bonds. This suggests that these interactions should be stronger than normal H-bonds, in view of the fact that there is a linear correlation between  $\rho_b$  and H-bond energy [34]. This is in agreement with the calculated H-bond energies of these molecules, which are about 12.5 kcal/mol (normal H-bonds are generally regarded as those with strengths of about 3–5 kcal/mol [35,36]).

$\nabla^2\rho_b$  is related to the bond nature by the local expression of the virial theorem [30]:

$$\frac{1}{4}\nabla^2\rho_b = 2G_b + V_b \quad (1)$$

$G_b$  is always positive and  $V_b$  is always negative, and consequently, the sign of  $\nabla^2\rho_b$  is determined by which energy is in excess over the virial ratio of 2:1 of  $G_b$  to  $V_b$ . In covalent interactions, the electron density at the BCP is tightly bound and compressed over its average distribution. Therefore for covalent bonds, a negative value of  $\nabla^2\rho_b$  is expected, because  $V_b$  dominates in Eq. (1). In electrostatic interactions the electronic charge is expanded relative to its average distribution, the kinetic energy density is dominant and  $\nabla^2\rho_b$  is positive at the BCP. On the other hand, Cremer and Kraka [37] showed that in covalent bonds the electronic energy density, defined as

$$H_b = G_b + V_b \quad (2)$$

should be negative at the BCP. In other words, in covalent bonds  $|V_b| > G_b$ . Now, consider a special case in which  $|V_b| < 2G_b$  while  $|V_b| > G_b$ . This situation provides a positive  $\nabla^2\rho_b$  (electrostatic interaction) and a negative  $H_b$  (covalent interaction). Taking a closer look at the values of  $G_b$  and  $V_b$  of studied molecules (Table 5) reveals that  $|V_b| < 2G_b$  and  $|V_b| > G_b$  for them. So it seems that these H-bonds show both electrostatic ( $\nabla^2\rho_b > 0$ ) and covalent ( $H_b < 0$ ) characters simultaneously. Therefore, they should be termed as partially covalent and partially electrostatic, in contrast to normal hydrogen bonds, which are electrostatic in nature. This is a characteristic which has been observed previously for strong and very strong H-

bonds [34]. Consequently, both calculated interaction energies and QTAIM parameters indicate that there are strong intramolecular H-bonds between nitrogen and hydrogen in the studied molecules.

#### 4. Conclusion

In conclusion we synthesized the two new Schiff base compounds **1** and **2** in simple procedures. The crystal structure of them was determined by single crystal X-ray analysis. In addition theoretical studies used to find intramolecular interactions. The resulting experimental and theoretical data from Schiff base compounds **1** and **2** reveal that there are strong intramolecular hydrogen bonds between the proton of phenols and nitrogen of imines.

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#### Appendix A. Supplementary material

CCDC 916304 & 916303 contains the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.molstruc.2013.09.026>.

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