### Accepted Manuscript

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

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PII: DOI: Reference:	S0022-2860(13)00801-6 http://dx.doi.org/10.1016/j.molstruc.2013.09.026 MOLSTR 20023
To appear in:	Journal of Molecular Structure
Received Date: Revised Date: Accepted Date:	<ul><li>13 July 2013</li><li>18 September 2013</li><li>18 September 2013</li></ul>



Please cite this article as: G. Grivani, V. Tahmasebi, K. Eskandari, A.D. Khalaji, G. Bruno, H.A. Rudbari, 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, *Journal of Molecular Structure* (2013), doi: http://dx.doi.org/10.1016/j.molstruc.2013.09.026

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1	Synthesis, characterization, crystal structure determination and
2	computational study of the two new bidentate O, N Schiff bases derived
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4	groups
5	
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17	
18	Abstract
19	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 21 22 single-crystal X-ray diffraction. They crystallize in the triclinic system, space group P-1. Both 23 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 24 25 intramolecular interactions and investigate their chemical nature. The results show that in both 26 of the compounds 1 and 2, there is a hydrogen bonding between nitrogen of imine and oxygen 27 of phenol which is considerably stronger than normal hydrogen bonds. In addition, it has been 28 shown that these hydrogen bonds are partially covalent and partially electrostatic in nature, in 29 contrast to normal hydrogen bonds, which are usually considered as electrostatic interactions.

30

31 *Keywords:* Schiff-base · Spectroscopy · Single-crystal · Hydrogen bond · DFT

32

#### 33 **1. Introduction**

Azomethines (known as Schiff-bases), having imine groups (-C=N-), are formed by 34 the condensation reaction of primary amines with aldehydes or ketones. They are some of the 35 36 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 37 38 industrial purposes such as pigments, catalysts, intermediates in organic synthesis and as 39 polymer stabilizers [3]. Schiff bases are an important class of compounds in both the 40 medicinal and pharmaceutical fields [4-6] and have also found to exhibit a broad range of 41 biological activities, including antifungal, antibacterial, antimalarial, antiproliferative, anti-42 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 43

the role of such complexes in providing synthetic interesting models for the metal-containingsites in metallo-proteins and -enzymes [9-17].

46 We started to investigate the synthesis, characterization, crystal structure determination of some new bidentate (O,N) Schiff bases ligands derived from substituted 47 salicylaldehydes and some amines containing alkyl halide pendant groups and their metal 48 49 complexes[18, 19]. In this research we describe the synthesis, characterization, crystal 50 structure determination and computational study of 2-{(E)-[2-(bromoethyl)imino]methyl}-4and 2-{(E)-[2-(chloroethyl)imino]methyl}-4-bromo (2) and Schiff base 51 bromo (1) 52 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 53 focused on the electron density and it's Laplacian, kinetic energy density, potential energy 54 55 density and energy density from Bader's quantum theory of atoms in molecules (QTAIM) 56 [20].

57

<Scheme 1>

58

### 59 **2. Experimental**

60

#### 61 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 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

66 AVANCE spectrometer at 500 MHz. All chemical shifts are reported in  $\delta$  units downfield 67 from TMS.

68

69 2.2. Preparation of the  $2-\{(E)-[2-(bromoethyl))imino]methyl\}-4-bromophenol(1)$ 

70 To a 250 ml round bottom flask containing 150 ml absolute methanol were added 10 71 mmol of 4-bromo-2-hydroxy benzaldehyde, 10 mmol of 2-bromoethyl ammonium 72 hydrobromide and 10 mmol of NaOH and the content was refluxed with stirring for 4 h. After 73 evaporating the solvent, the yellow precipitate was collected and washed with slightly cooled 74 water and then with 1:1 mixture of n-hexane and dichloromethane. Yield: 2.24 g (73%). The 75 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: 76 77 C, 35.18; H, 2.93; N, 4.56 %. IR (KBr pellet, cm<sup>-1</sup>): 3350-3480 (b, O-H, phenolic), 2840-78 3050 (w, C-H aliphatic and aromatic), 1636 (s, C=N), 1436, 1481, 1581, 1602 (m, C=C), 79 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 80 (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: 81 -N-CH<sub>2</sub>-).

82

### 83 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 2bromoethyl 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>-).

93 2.4. X-ray structure determination

A Single crystal of the dimension 0.49 mm  $\times$  0.15 mm  $\times$  0.10 mm of 1 and 0.43 mm  $\times$ 94 0.39 mm  $\times$  0.10 mm of 2 were chosen for X-ray diffraction study. Diffraction data were 95 measured on a Bruker-Nonius X8 ApexII diffractometer equipped with a CCD area detector 96 by using graphite-monochromated Mo Ka radiation (k = 0.71073 Å) generated from a sealed 97 tube source. Data were collected and reduced by smart and saint software [21] in the Bruker 98 package. The structures were solved by direct methods [22] and then developed by least 99 squares refinement on  $F^2$  [23, 24]. All non-H atoms were placed in calculated positions and 100 refined as isotropic with the "riding-model technique". Crystallographic data and details of 101 the data collection and structure solution and refinements are listed in Table 1. Bond 102 distances, angles and torsion angles are listed in Table 2. 103

### <Tables 1 and 2>

105

104

#### 106 **3. Results and Discussion**

107 3.1. Synthesis and characterization

By reaction of eqimolar of 4-bromo-2-hydroxybenzaldehyde with 2-bromooethyl 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>HNMR 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 determined by FT-IR and <sup>1</sup>H-NMR spectra and approved with crystal structure determination by X-ray analysis.

117

118 3.2. FT-IR spectrum

The characteristic band in the FT-IR spectrums of **1** and **2** is the appearance of the strong band at 1636 cm<sup>-1</sup>, attributed to the -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 2800-3050 cm<sup>-1</sup>, and strong bands for the aromatic C=C stretching bonds in the region 1300-1500 cm<sup>-1</sup> [25,26]. Fig. 1 shows the FT-IR spectrums of **1** and **2**.

125

#### <Fig. 1>

126

### 127 *3.3.* <sup>1</sup>*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 <sup>1</sup>HNMR 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 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 (H–C=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  $-N-CH_2-$  and  $-CH_2Cl$  or -CH<sub>2</sub>Br are showed a triplet peak in 3.6- 4-1 ppm, for Schiff base compounds 1 and 2. Fig. 2 shows the <sup>1</sup>H-NMR spectrum of the 1.

139

### <Fig. 2>

#### 140 *3.4. Thermal studies*

141 The TGA/DTG/DTA profiles of the two compounds 1 and 2 are given in the Fig. 3. 142 Because of existing the different functional groups on the two compounds 1 and 2, they are 143 decomposed in four stages about the range of 90-600 °C but the thermal decomposition trends 144 of them are not the same.

145

<Fig. 3>

146

### 147 *3.5. Description of the crystal structures*

148 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. 149 All bonds distances and angles are normal and are in good agreement with those reported in 150 similar Schiff-base compounds [25,26]. The C3=N1 bond length of 1.270(3) Å in 1, and 151 1.265(3) Å in 2 conform to the value for a double bond, while the C2-N1 bond length of 152 1.4557(3) Å in 1, and 1.447(3) Å in 2 conform to the value for a single bond, like in similar 153 154 Schiff-base compounds [22,23]. The bond angle C4-C3-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 155 156 the bond angle C3-N1-C2 is 119.3(2) and  $119.5(2)^{\circ}$ , respectively in 1 and 2, which is consistent with the  $sp^2$  hybrid character of N1 atom. 157

158

#### <Figs. 4 and 5>

159	Ortho position to the imine group of Schiff-base occupied with the OH is interesting
160	due to the existence of O-H…N hydrogen bond and possibility of tautomerism between enol-
161	imine and keto-amine form in 2-hydroxy Schiff bases [27,28]. In the structures of Schiff base
162	1 and 2, there is an intramolecular O1-H1…N1 hydrogen bond (Figs. 6, 7 and Table 3) as in
163	the Schiff bases derived from salicylaldehyde that always form the O-H…N type of hydrogen
164	bonding, regardless of the nature of the N substituent [29,30]. Molecular packing of $1$ and $2$
165	can be viewed molecules held together by various intermolecular hydrogen bonds (Figs. 6, 7
166	and Table 3).

167

### <Figs. 6 and 7>

168

<Table 3 >

169

#### 170 *3.6. Theoretical studies*

It is well known that the quantum theory of atoms in molecules (QTAIM) provides a 171 powerful tool for characterizing the chemical bonds [31, 32]. This theory uses the electron 172 density as an information source to describe atoms, bonds and molecules. So, to obtain the 173 174 electron densities, Gaussian 03 program [33] has been used to generate electronic wavefunctions. To investigate intramolecular interactions, molecular geometries have 175 176 optimized at B3LYP/6-311++G(d, p). Geometrical parameters (bond lengths, angels and 177 dihedrals) of the studied compounds have been listed in Table 2. QTAIM calculations have 178 carried out with AIMAll suite of programs [34]. In this part of article, we will use 179 terminology of QTAIM, which has been reviewed elsewhere [31, 32].

180

#### <Table 2>

181

182 In QTAIM viewpoint, a chemical bond (including covalent, ionic, van der Waals, 183 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 184 single molecules of this work have been shown in Fig. 8. As indicated, in addition to usual 185 186 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. 187 188 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 189 electron density,  $\nabla^2 \rho_b$ , kinetic energy density,  $G_b$ , potential energy density,  $V_b$ , and 190 electronic energy density,  $H_b$ , at the BCP are the parameters that are usually used to 191 192 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 193  $\nabla^2 \rho_b$  and  $H_b$  at the BCP [2]. These values for the BCP of the H-bonds in the compounds of 194 the current work have been listed in Table 6. The values of  $\rho_b$  of these compounds are 195 slightly larger than that of normal hydrogen bonds. This suggests that these interactions 196 should be stronger than normal H-bonds, in view of the fact that there is a linear correlation 197 between  $\rho_b$  and H-bond energy [35]. This is in agreement with the calculated H-bond 198 energies of these molecules, which are about 12.5 kcal/mol (normal H-bonds are generally 199 200 regarded as those with strengths of about 3-5 kcal/mol [36, 37]. 201 <Fig. 8> 202 <Table 6>

203

204

 $\nabla^2 \rho_b$  is related to the bond nature by the local expression of the virial theorem [31]:

$$\frac{1}{4}\nabla^2 \rho_b = 2G_b + V_b \tag{1}$$

 $G_b$  is always positive and  $V_b$  is always negative, and consequently, the sign of  $\nabla^2 \rho_b$  is 206 determined by which energy is in excess over the virial ratio of 2:1 of  $G_b$  to  $V_b$ . In covalent 207 interactions, the electron density at the BCP is tightly bound and compressed over its average 208 distribution. Therefore for covalent bonds, a negative value of  $\nabla^2 \rho_b$  is expected, because  $V_b$ 209 is dominates in equation 1. In electrostatic interactions the electronic charge is expanded 210 relative to its average distribution, the kinetic energy density is dominant and  $\nabla^2 \rho_b$  is 211 positive at the BCP. On the other hand, Cremer and Kraka [38] showed that in covalent bonds 212 213 the electronic energy density, defined as

214 
$$H_b = G_b + V_b \tag{2}$$

should be negative at the BCP. In other words, in covalent bonds  $|V_b| > G_b$ . Now, consider a 215 special case in which  $|V_b| < 2G_b$  while  $|V_b| > G_b$ . This situation provides a positive  $\nabla^2 \rho_b$ 216 (electrostatic interaction) and a negative  $H_h$  (covalent interaction). Taking a closer look at the 217 values of  $G_b$  and  $V_b$  of studied molecules (Table 5) reveals that  $|V_b| < 2G_b$  and  $|V_b| > G_b$  for 218 them. So it seems that these H-bonds show both electrostatic  $(\nabla^2 \rho_b > 0)$  and covalent 219  $(H_b < 0)$  characters simultaneously. Therefore, they should be termed as partially covalent 220 221 and partially electrostatic, in contrast to normal hydrogen bonds, which are electrostatic in 222 nature. This is a characteristic which has been observed previously for strong and very strong 223 H-bonds [35]. Consequently, both calculated interaction energies and QTAIM parameters 224 indicate that there are strong intramolecular H-bonds between nitrogen and hydrogen in the studied molecules. 225

r	2	c
Z	Z	σ

#### <Table 5>

С	2	7
2	2	1

#### 4. Conclusion 228

229 In conclusion we synthesized the two new Schiff base compounds 1 and 2 in simple 230 procedures. The crystal structure of them was determined by single crystal X-ray analysis. In 231 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 232 strong intramolecular hydrogen bondings between the proton of phenols and nitrogen of 233 imines. 234 NAS

235

#### 236 Appendix A. Supplementary data

237 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 238 from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, 239 240 UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

241

#### 242 Acknowledgments

243 G. Grivani, V. Tahmasebi, K. Eskandari and A.D. Khalaji are grateful to the Damghan 244 University and Golestan University for financial support. 245

#### 246 References

247 [1] M. Shebl, Spectrochim Acta A. 70 (2008) 850-859.

- 248 [2] M. Hobady, T.D. Smith, Coord. Chem. Rev. 9 (1973) 311-337.
- [3] M. Cleiton, L. da Silva Daniel, V.M. Luzia, B.A. Rosemeire, A. de Resende Maria,
- 250 V..B.C Martins, A. de Fa´ tima, J. Adv. Res. 2 (2011) 1-8.
- 251 [4] A.A. Azza, J. Coord. Chem. 59 (2006) 157-176.
- [5] M.S. Karthikeyan, D.J. Parsad, B. Poojary, K.S. Bhat, B.S. Holla, N.S. Kumari, Bioorg.
- 253 Med. Chem. 14 (2006) 7482-7489.
- 254 [6] K. Singh, M.S. Barwa, P. Tyagi, Eur. J. Med. Chem. 41 (2006) 147-153.
- 255 [7] D.N. Dhar, C.L. Taploo, J. Sci. Ind. Res. 41 (1982) 501-506.
- [8] P. Przybylski, A. Huczynski, K. Pyta, B. Brzezinski, F. Bartl, Curr. Org. Chem.13 (2009)
  124-148.
- 258 [9] D.N. Dhar, C.L. Taploo, J. Sci. Ind. Res. 41 (1982) 501-506.
- [10] S. Ren, R. Wang, K. Komastu, P.B. Krause, Y. Zyrianov, C.E. Mckenna, C. Csipke,
- 260 Z.A. Tokes, E.J. Lien, J. Med. Chem, 45 (2002) 410-419.
- [11] A.A. Khandar, S.A. Hosseini-Yazdi, S.A. Zarei, Inorg. Chim. Acta. 358 (2005) 32113217.
- 263 [12] P.K. Mascharak, Coord. Chem. Rev. 225 (2002) 201-214.
- 264 [13] J.G. Muller, L.A. Kayser, S.J. Paikoff, V. Duarte, N. Tang, R.J. Perez, S.E. Rokita, C.J.
  265 Burrows, Coord. Chem. Rev. 185–186 (1999) 761-774.
- 266 [14] D.P. Kessissoglou, Coordin. Chem. Rev. 185–186 (1999) 837-858.
- 267 [15] J.W. Pyrz, A.L. Roe, L.J. Stern, L. Que, J. Am. Chem. Soc. 107 (1985) 614-620.

- 268 [16] V.E. Kaasjager, L. Puglisi, E. Bouwman, W.L. Driessen, J. Reedijk, Inorg. Chim. Acta .
- 269 310 (2000) 183-190.
- 270 [17] A.S. Al-Shihri, Spectrochim. Acta A. 60 (2004) 1189-1192.
- 271 [18] G. Grivani, A.D. Khalaji, V. Tahmasebi, K. Gotoh, H. Ishida, Polyhedron 31, 265-271
- 272 (2012).
- [19] G. Grivani, G. Bruno, H. Amiri Rudbari, A.D. Khalaji, P. Pourteimouri, Inorg. Chem.
  Commun. 18 (2012) 15-20.
- 275 [20] R.W.F. Bader, Atoms in Molecules: A Quantum Theory () Oxford University Press,

276 Oxford, 1990.

- [21] AXS Bruker Inc., SMART, Version 5.060 and SAINT, Version 6.02, Madison,
  Wisconsin, USA, 1999.
- [22] M.C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G.L. Cascarano, L. De Caro, C.

280 Giacovazzo, G. Polidori, R. Spagna, J. Appl. Crystallogr. 38 (2005) 381-388.

- [23] G.M. Sheldrick, SHELXL97, Program for Crystal Structure Refinement, University of
- 282 Göttingen, Germany, 1997.
- [24] L.N. SHELXT, Version 5.10, Bruker Analytical X-ray Inc., Madison, WI, USA, 1998.
- 284 [25] A.D. Khalaji, K. Fejfarova, M. Dusek, Acta. Chim. Slov. 57 (2010) 257-261.
- [26] A.D. Khalaji, A. Najafi Chermahini, K. Fejfarova, M. Dusek, Struct Chem 21 (2010)153157.
- [27] H. Unver, M. Yildiz, B. Dulger, O. Ozgen, E. Kendi, T.N. Durlu, J. Mol. Struct. 737
  (2005) 159-164.

- 289 [28] H. Unver, M. Yildiz, H. Ozbay, T.N. Durlu, Spectrochim. Acta A. 74 (2009) 1095-1099.
- 290 [29] A. Elmali, Y. Elerman, C.T. Zeyrek, J. Mol. Struct. 443 (1998) 123-130.
- 291 [30] A. Elmali, Y. Elerman, J. Mol. Struct. 442 (1998) 31-37.
- [31] R.W.F. Bader (1990) atoms in Molecules: A Quantum Theory. Oxford University,
  Oxford.
- [32] P. Popelier, Atoms in Molecules; an Introduction. Prentice Hall, UK, 2000.
- [33] M.J. Frisch, G.W. Trucks, H.B. Schlegel, GE Scuseria, M.A. Robb, J.R. Cheeseman, Jr.
- JA. Montgomery, T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J.
- 297 Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H.
- 298 Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T.
- 299 Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B.
- 300 Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J.
- Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P.
- 302 Salvador, J.J. Dannenberg, V.G. Zakrzewski, A. Daniels, M.C. Strain, O. Farkas, D.K.
- 303 Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S.
- 304 Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi,
- 305 R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M.
- 306 Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople,
- 307 Gaussian 03 Revision B.03 Gaussian, Inc. Wallingford CT, 2004.
- 308 [34] Keith TA, Gristmill TK Software, AIMAll (Version 11.02.27) Overland Park KS, USA
  309 (aim.tkgristmill.com), 2011.
- 310 [35] A.H. Pakiari, K. Eskandari, J. Mol. Struct (THEOCHEM). 759 (2006) 51-60.

- 311 [36] J. Emsley, Chem. Soc. Rev. 9, 91-124 (1980).
- 312 [37] G.A. Jeffrey, An Introduction to Hydrogen Bonding, Oxford University Press, Oxford,

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- 313 1997.
- 314 [38] D. Cremer, E. Kraka, Angew. Chem. 23 (1984) 627-628.
- 315 **Table 1**
- 316 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	Р	Р
Т(К)	296 (2)	296 (2)
a (Å)	4.6637 (3)	4.6065 (2)
<i>b</i> (Å)	9.0052 (5)	8.8898 (5)
<i>c</i> (Å)	12.5622 (7)	12.4802 (7)
$\alpha$ (deg)	84.600 (2)	84.992 (3)
$\beta$ (deg)	83.333 (2)	83.703 (2)
γ (deg)	89.713 (2)	88.848 (3)
$V(\text{\AA}^3)$	521.68 (5)	506.02 (5)
Ζ	2	2
$F_{000}$	296	260

$D_{\rm x}$ (Mg m <sup>-3</sup> )	1.954	1.723
$\mu (\mathrm{mm}^{-1})$	7.73	4.28
$ heta_{\min}, \  heta_{\max}$	2.9, 26.0	2.3, 25.7
$T_{\min}$ , $T_{\max}$	0.524, 0.745	0.564, 0.745
Measured reflections	4649	3471
Independent reflections	2021	1901
Reflection with $I > 2\sigma(I)$	1717	1561
$R_{\rm int}$	0.016	0.014
S	1.00	0.96
$R[F^2 > 2\sigma(F^2)]$	0.027	0.027
$wR(F^2)$	0.066	0.079
Parameters	119	119
$\Delta \rho_{\text{max}}, \Delta \rho_{\text{min}} (e \text{\AA}^{-3})$	0.39, -0.58	0.47, -0.21
Index range	$-5 \le h \le 5$	$-5 \le h \le 5$
	$-10 \le k \le 11$	$-10 \le k \le 6$
	-15 ≤ <i>l</i> ≤ 15	-15 ≤ <i>l</i> ≤ 15
6		
Table 2		

### 320 Selected and Calculated bond distances (Å), angles (°) and torsion angles (°)

Br(2)-C(1)	1.954(3)	1.974		
	1	1*	2	2*
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\*

### 

### **Table 3**

molecule	intraction	<i>D</i> —H····A	<i>D</i> —Н	H···A	$D \cdots A$	<i>D</i> —H···A
	Intramolecular	01—H1…N1	0.820	1.845	2.575	147.681
1	Intermolecular	C2—H2b…O1	0.969	2.818	3.612	139.647
	Intermolecular	C1—H1a…Br2	0.970	3.127	3.803	128.169
	Intramolecular	O1—H1…N1	0.820	1.851	2.580	147.344
2	Intermolecular	C5—H5…Br1	0.930	3.488	4.039	120.430
					0	

326 **Table 4** 

325

327 QTAIM parameters (in *a.u.*) at the BCP of intramolecular  $N \cdots H$  hydrogen bonds

-	Molecule	$oldsymbol{ ho}_b$	$ abla^2  ho_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
	2	0.040	0.111	0.050	-0.044	-0.000
328		0				

329 **Table 5** 

330 Theoretical geometries of intramolecular hydrogen bonds (Bond distances are in Angstrom

	D—H···A	<i>D</i> —H	H···A	$D \cdots A$	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

and angles are in degree)





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







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







Fig. 8. Molecular graphs of 1 (a) and 2 (b), red points indicate the bond critical points (BCPs) 403 between bonded atoms. 404

- 405 Highlights
- 406 . Two new Schiff base compounds have been synthesized.
- 407 . 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. 408
- . There is a strong hydrogen bonding between nitrogen of imine and oxygen of phenol. , he 409
- 410 .They are partially covalent and partially electrostatic in nature.