Neutral and Ionic Hydrogen Bonding in Schiff Bases

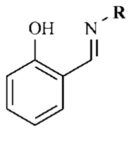
Paulina M. Dominiak,[a] Eugeniusz Grech,[b] Gordon Barr,[c] Simon Teat,[d] Paul Mallinson,[c] and Krzysztof Woźniak*[a]

Abstract: Low-temperature, high-resolution X-ray studies of charge distributions in the three Schiff bases, the dianil of 2-hydroxy-5-methylisophthaldehyde, 3,5-dinitro-*N*-salicylidenoethylamine and 3-nitro-*N*-salicylidenocyclohexylamine, have been carried out. These structures exhibit interesting weak interactions, including two extreme cases of intramolecular hydrogen bonds that are ionic N^{+}–H···O^{-} and neutral O–H···N in nature. These two types of hydrogen bond reflect differences in geometrical parameters and electron density distribution. At the level of geometry, the neutral O–H···N hydrogen bond is accompanied by an increase in the length of the C(1)–O(1) bond, opening of the *ipso*-C(1) angle, elongation of the aromatic C–C bonds, shortening of the C(7)–N(2) bond and increased length of the C(1)–C(7) bond, relative to the ionic hydrogen bond type. According to the geometrical and critical point parameters, the neutral O–H···N hydrogen bond seems to be stronger than the ionic ones. There are also differences between charge density parameters of the aromatic rings consistent with the neutral hydrogen bond being stronger than the ionic ones, with a concomitant reduction in the aromaticity of the ring. Compounds with the ionic hydrogen bonds show a larger double-bond character in the C–O bond than appears in the compound containing a neutral hydrogen bond; this suggests that the electronic structure of the former pair of compounds includes a contribution from a zwitterionic canonical form. Furthermore, in the case of ionic hydrogen bonds, the corresponding interaction lines appear to be curved in the vicinity of the hydrogen atoms. In the 3-nitro-*N*-salicylidenocyclohexylamine crystal there exists, in addition to the intramolecular hydrogen bond, a pair of intermolecular O···H interactions in a centrosymmetric dimer unit.

Keywords: electron density · hydrogen bonds · Schiff bases · topological analysis

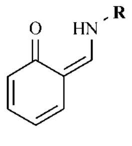
Introduction

Schiff bases[1–5] have the general formula Ar–CH=N–R and they are products of the condensation of aromatic aldehydes or ketones with primary amines. The *o*-hydroxy derivatives of these compounds are of particular interest due to an asymmetric intramolecular hydrogen bond formed between the oxygen and nitrogen atoms. Depending on the position of the hydrogen atom in this O···H···N bond, the *o*-hydroxy Schiff bases exhibit two tautomeric forms: the OH form (**A**) or the NH form (**B**). Additionally, the NH tautomer can exist in the ketoenamine form **B** or the zwitterionic form **C**.



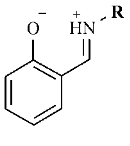
A

enol-imine



B

keto-enamine



C

zwitterionic

This hydrogen bond forms a six-membered chelate ring. The unsaturated –CH=N– bond permits π-electronic coupling between the acidic and basic centres of the molecule. Additionally, this ring is planar in many *o*-hydroxy Schiff bases. For these reasons it is called a pseudoaromatic chelate ring.[6] There are also nonplanar Schiff bases.[7]

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Supporting information for this article is available on the WWW under http://www.chemeurj.org or from the author: Monopole charges, κ′ and κ″ values obtained from the refinement, critical point data, multipole population coefficients, definitions of local axes, bond lengths and angles for **1**, **2** and **3**.

In fact there is a proton-transfer equilibrium between the OH and NH tautomers. *o*-Hydroxy Schiff bases exhibit ground and excited state proton-transfer processes both in solution and in the solid state.[8] This equilibrium is known to be dependent on the solvent polarity as well as on temperature and light.

Moreover, this proton tautomerisation is closely related to solvato-, thermo- and photochromic properties exhibited by *o*-hydroxy Schiff bases.[9–14] In the first instance this phenomenon was found only in salicylideneanilins. The products of condensation of salicylaldehydes with anilines and also with aliphatic amines show intermolecular proton-transfer equilibrium and double fluorescence.[15, 16]

Proton transfer causes a change in the π-electron system. This means that the electronic and the protonic states are actually strongly coupled.[17] On the basis of structural studies on photo- and thermochromic salicylaldimine derivatives, it was concluded that there are significant differences in the packing of the Schiff molecules in the crystal lattices. Thermochromism is associated with a change in the π-electron configuration induced by proton transfer. This can take place in the ground state and requires a planar molecular system. The nonplanar molecules exhibit photochromic properties.[10–14, 18, 19]

In most Schiff bases studied so far in the solid state the proton is localised at the oxygen atom. However, in some cases the proton position is disordered over two sites—at the N and O atoms.[7] There are also some examples of Schiff bases with hydrogen at the nitrogen atom.[20, 21] It is of interest to consider the factors which influence the properties of intramolecular hydrogen bonds in Schiff bases. It has been previously suggested that the position of the proton transfer equilibrium in anils of aromatic α-hydroxyaldehydes is controlled by the acid–base characteristics of both the enol and imine moieties.[8] Generally, it is assumed that π-electron delocalisation leads to hydrogen-bond strengthening, which is characteristic of so-called resonance-assisted hydrogen bonding.[22, 23] Also, considerable strengthening of the intramolecular O–H···N hydrogen bridge was achieved as a result of the steric shortening of the hydrogen bridge.[24]

The question arises as to which form, the keto- or zwitterionic one, better explains the NH tautomer. Ogawa and co-workers indicate that in the solid state the NH tautomer is predominantly in the zwitterionic form, which is considerably stabilised by electrostatic intermolecular interactions.[9]

The process of proton tautomerisation is fundamental not only to understanding the chemical behaviour of these interesting systems, but also has some technical implications. The proton-exchanging materials can be utilised for designing molecular electronic devices.[8] Due to their physicochemical properties, Schiff base molecules can be used as elements for constructing optical switches or optical memory devices.[24]

Different techniques have been used to study Schiff bases so far. For example, the structures of Schiff bases have been examined crystallographically by using both X-ray[16, 21, 25] and neutron, single-crystal diffraction methods as well as IR, UV-visible and multinuclear magnetic resonance techniques in both solid and liquid phases.[6, 26, 27] A detailed vibrational analysis based on ab initio calculations, infrared (IR), Raman (R) and inelastic neutron scattering studies, over the whole frequency range has been reported.[28] Schiff bases have also been investigated by means of absorption, emission and nanosecond spectroscopies in different protic solvents at different temperatures.[29] The proton-transfer rate in a crystalline phase was estimated by femtosecond time-resolved fluorescence spectroscopy.[30]

The tautomerism in the solid phase has been studied by near-edge X-ray absorption fine structure (NEXAFS) spectroscopy at the N and O K-edges and X-ray photoelectron spectroscopy (XPS) in the N1s and O1s regions for *N*-salicylideneaniline derivatives.[17]

The photochromic properties have been studied by time-dependent fluorescence spectroscopy, UV-visible absorption, and theoretical chemistry calculation methods.[31, 32] Solid-state electronic absorption, fluorescence emission and ^{13}C CP/MAS spectroscopies have been applied to a series of aromatic Schiff bases displaying both ground and excited state intramolecular proton transfer phenomena.[33]

The dipole moments of a series of Schiff bases in CCl_4 have been measured. The influence of the substituents on the conformation of the molecules, the intramolecular hydrogen-bond energy and tautomerism were studied by means of semiempirical PM3, AM1 and ab initio methods.[34–39]

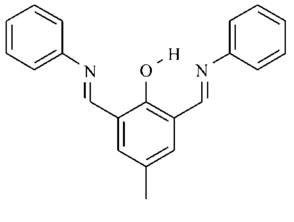
The deuterium isotope effects on chemical shifts have been used to establish the presence and the position of the equilibrium.[40–42] Also the Mannich bases, reference compounds with a saturated $-CH_2-NH-$ bond, have been studied.[43]

The aim of our work is to present structural and electronic characteristics of two extreme cases of hydrogen bonding—with the hydrogen atom at oxygen or at nitrogen—with particular reference to the hydrogen-bonding region and the aromatic moiety. Because of the mobility of the electrons, one can expect the effects of any differences to be transmitted to the far end of the molecules.

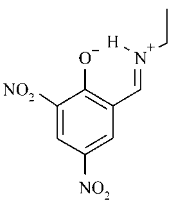
The following molecules are the subject of the study: the dianil of 2-hydroxy-5-methyl-isophth-aldehyde (**1**),[44] 3,5-dinitro-*N*-salicylidenoethylamine (**2**)[20] and 3-nitro-*N*-salicylidenocyclohexylamine (**3**). The structures of these molecules are shown in Figure 1.

Compound **1** is known to contain—as is typical for most Schiff bases—a neutral O–H···N hydrogen bond.[44] According to CSD[45] searches, about 90% of all known Schiff base structures exhibit such hydrogen bonding. We contrast this structure with two examples of Schiff bases containing an ionic $O^-\cdots H-N^+$ hydrogen bond, which seems to be imposed

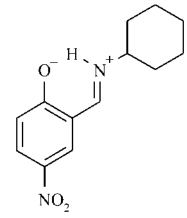
Abstract in Polish: *Parametry charakteryzujące rozkłady gęstości elektronowych (oraz geometrię) w zasadach Schiffa posiadających neutralne O–H···N oraz jonowe [N⁺-H··· O⁻] wiązanie wodorowe świadczą o tym, że wiązanie O–H···N jest mocniejsze od jonowego wiązania wodorowego. Ten zadziwiający rezultat potwierdzony jest również wartościami lokalnych gęstości energii kinetycznej i potencjalnej uzyskanymi dla w/w wiązań wodorowych.*



1



2



3

by through-molecule interactions between the $-NO_2$ group(s) present in **2** and **3** in the *para* and/or *ortho* position(s), and resonance-assisted hydrogen bonding. Our aim is to find experimentally any differences in electronic and geometric structures of the ionic and neutral Schiff bases resulting from the presence of different electron-donating (−Me) and electron-withdrawing ($-NO_2$) groups.

Results and Discussion

Details of the final *R* factors, goodness of fit, and the ranges of residual density over the whole asymmetric units are given in Table 1. All bonds pass Hirschfeld's rigid bond test,[46] with the largest $\Delta_{A,B}$ value of 0.001 Å^2 for C(16)–(17) in **1**.

The hydrogen atoms involved in hydrogen bonding carry a positive charge in the range 0.1–0.4 e. In fact the last value (for **2**) is the most positive of all hydrogens in the three molecules. The charges at the imine nitrogen atom are close to zero for **2** and about −0.2 e for **1** and **3**. In one case of the ionic hydrogen bonds (**2**), most of the aromatic atoms are negatively charged (ca. −0.3 e, see Supporting Information) and, in general, are close to zero within the level of errors for **1** and **3**.

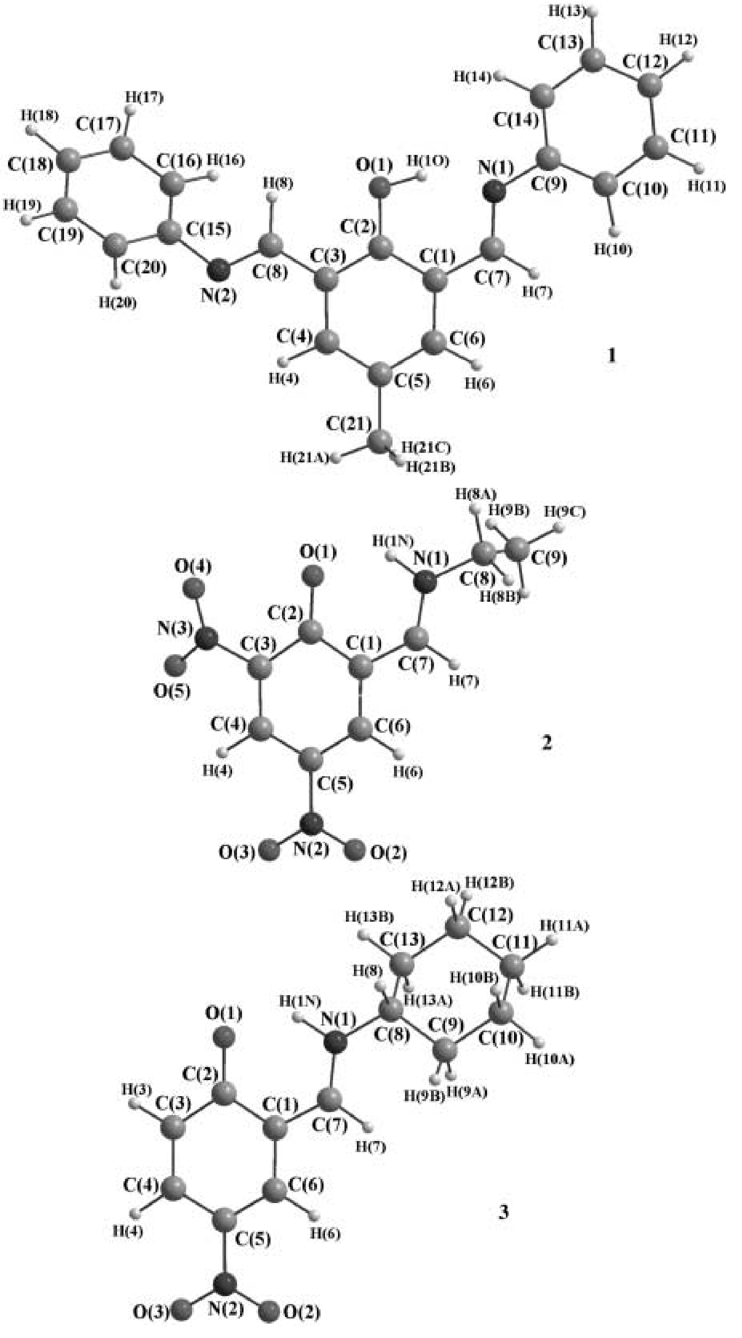


Figure 1. Labelling of atoms in the compounds studied: **1**, **2** and **3**.

Bond lengths: The bond lengths are given in Figure 2. Surprisingly enough, according to the numerical values of bond lengths and interatomic distances, the intramolecular neutral O–H···N hydrogen bond in **1** seems to be stronger than the intramolecular ionic hydrogen bonds in **2** and **3**. It has a shorter donor acceptor distance (2.5626(5) Å) than those of the ionic hydrogen bonds in **2** and **3** (2.6379(5) and 2.6668(5) Å, respectively). Also the H···acceptor distances are in line with this conclusion (1.665(1) Å for H···N and 1.849(1) and 1.869(1) Å for H···O distances). Similar values of structural parameters are obtained for all Schiff bases with neutral and ionic hydrogen bonds that can be retrieved from the Cambridge Structural Database (CSD[45]); the average H···N and O···H distances are equal to 1.809 and 1.879 Å. The donor···acceptor distance is slightly shorter for the O–H···N hydrogen bond than for the ionic bonds (2.584 and 2.594 Å, respectively). There are also

Table 1. Crystal data.

	1	**2**	**3**
formula	$C_{21}H_{18}O_1N_2$	$C_9H_9O_5N_3$	$C_{13}H_{16}O_3N_2$
M_r	314.4	239.2	248.3
T [K]	100	100	100
λ [Å]	0.7107	0.7107	0.4839
crystal system	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a [Å]	8.5470(1)	8.1530(1)	6.245(2)
b [Å]	17.9520(2)	11.2840(2)	10.097(3)
c [Å]	10.4420(1)	11.3730(2)	10.873(4)
α [°]	90	90	67.23(3)
β [°]	91.084(1)	91.916(1)	83.46(2)
γ [°]	90	90	75.03(3)
V [Å^3]	1601.89(4)	1045.71(5)	610.6(4)
Z	4	4	2
ρ_{calcd} [Mg m^{-3}]	1.303	1.519	1.350
crystal size [mm^3]	0.40 × 0.30 × 0.30	0.45 × 0.35 × 0.25	0.40 × 0.30 × 0.30
$(\mathrm{Sin}\theta/\lambda)_{max}$	1.08	1.08	1.15
μ [cm^{-1}]	0.76	1.18	0.5
F(000)	664	496	264
index ranges	h:0,17; k:0,23; l: – 24,24	h:0,17; k:0,22; l: – 22,22	h:0,15; k: – 21,21; l: – 21,21
total reflections	16952	10921	13603
reflections observed	12126	8241	8009
R_{int}	0.035	0.036	0.034
N_{ref}/Nv	17.88	17.35	15.17
GOFw	1.7799	1.7466	0.6629
$R\{F\}$[a]	0.0426	0.0343	0.0288
$R\{F^2\}$	0.0526	0.0306	0.0351
$R_{all}\{F\}$	0.0977	0.0781	0.0731
$R_{all}\{F^2\}$	0.0603	0.0423	0.0453
$wR\{F\}$	0.0270	0.0197	0.0273
$wR\{F^2\}$	0.0513	0.0384	0.0499
DMSDA(max) [Å^2]	10	6	4
max (shift/esd)	0.0004	0.0056	0.012
largest diff. peak/hole [e Å^{-3}]	0.25/ – 0.22	0.29/ – 0.30	0.24/ – 0.21

[a] All R factors come from XD refinement.

differences between C(2)–O(1) and C(7)–N(1) bonds, and between the C(1)-C(2)-C(3) angles (Figure 2b).

One can expect quite reverse relations among structural parameters, because the ionic hydrogen bond should additionally be supported by strong partial charges of the donor and acceptor atoms. Thus, such hydrogen bonds should be stronger, because of stronger electrostatic interactions, than those not supported by charge.

Considering the bonds from the donor and acceptor atoms to their nearest neighbours, the C(2)–O(1) length (1.347(1) Å) is characteristic of a single bond in **1**, whereas in the cases where the oxygen is an acceptor the length (1.257(1) and 1.263(1) Å) is characteristic of a double bond. On the other hand for C(7)–N(1) there is no significant difference between the three lengths. The other bond to nitrogen varies in length in the manner consistent with the nature of the attached substituents, namely, aromatic for **1** and aliphatic for **2** and **3**.

There is also a certain regularity in the aromatic bond lengths: for **1**, in which the oxygen is the donor, all the bond lengths in the aromatic ring are equal; however, for the cases of ionic hydrogen bonds in **2** and **3**, C(1)–C(2) and C(2)–C(3) are significantly longer than the other four bonds (ca. 1.45 Å versus ca. or less than 1.40 Å).

Valence angles: The valence angles are given in Figure 3. It appears that the O–H···N hydrogen-bond angle (151.49(2)°) is larger than the $O^-\cdots H{-}N^+$ ones (130.58(2) and 131.66(2)° for **2** and **3**, respectively). This is again in line with the idea that the neutral hydrogen bond seems to be stronger than the ionic ones. It is difficult to compare the other internal pseudo-aromatic ring angles on account of different positions of the hydrogen atoms in the hydrogen bonds.

Also, the aromatic valence angles differ significantly. For example, the *ipso*-C(2) angle in the O–H form is 119.45(3)°, whereas in the N–H forms it has the smaller values of 113.92(3) and 116.18(3)°. This results from the amount of electron density associated with the bonds to C(2); this will be discussed in the next section. There is a corresponding effect seen in the alternation of increased and decreased values of the other ring angles, the sense of the alternation being reversed for the two extreme cases of hydrogen bonding.

Properties of the charge distribution: Recently Koch and Popelier have demonstrated that the theory of "atoms in molecules" (AIM)[47] can be used to characterise weak interactions on the basis of theoretical charge density (CD) distributions in the donor and acceptor molecules and in intermolecular regions.[48] Such an informative analysis of both the theoretical and experimental charge density is based upon the topological properties of the density $\rho(r)$. Any bonded pair of atoms has a bond path, that is, a line of the highest electron density linking them. The point on this line at which the gradient of ρ ($\nabla\rho(r)$) is equal to zero is termed the bond critical point (BCP), and the properties of the density ρ_b at this point give quantitative information about that bond's characteristics. A bond path between a pair of nonchemically bonded atoms is called an interaction line. The laplacian of the density ($\nabla^2\rho(r)$) contains a large amount of chemical information. Since this is the second derivative of the electron density, it indicates where the density is locally concentrated ($\nabla^2\rho(r) < 0$) and depleted ($\nabla^2\rho(r) > 0$), and hence graphically shows features such as bonds and lone pairs, which are not observable in $\rho(r)$ itself.

The values of ρ_b are shown in Figure 4. In compound **1** (O–H type of Schiff base) the electron densities at the C(2)–C(3) and C(2)–C(1) BCPs are 2.13(1) and

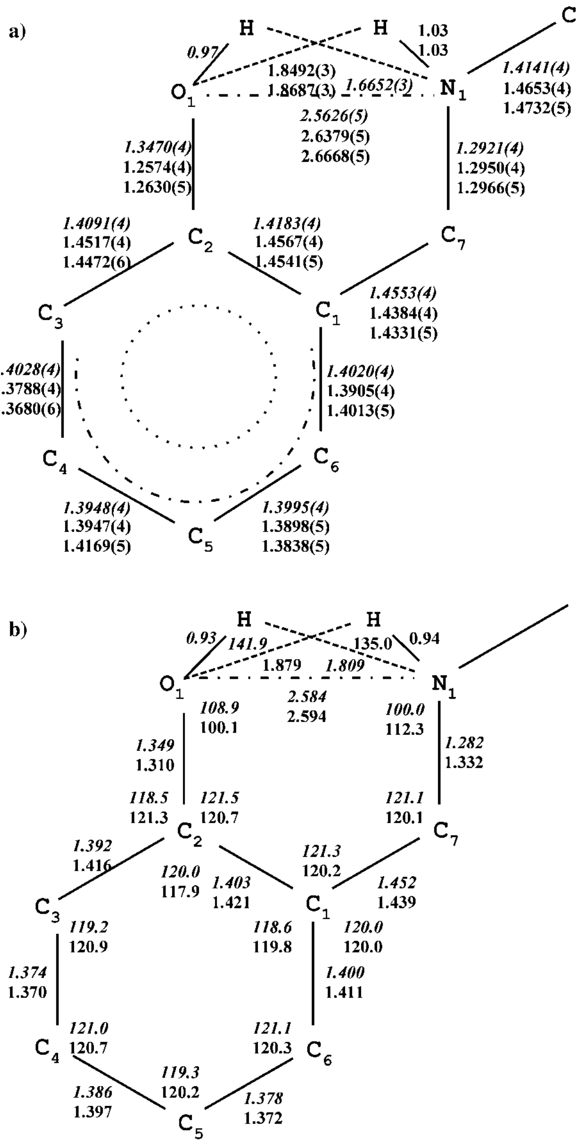


Figure 2. a) Bond lengths [Å] in **1** (in italics), **2** (second line) and **3** (third line) and b) average geometry obtained for the 283 molecular fragments of Schiff bases with O–H···N hydrogen bonding (in italics), and 22 structures of Schiff bases with ionic hydrogen bonding (second line).[45] In this and subsequent figures the subscripted number in the labelling corresponds to the number in brackets in Figure 1 (e.g., C_7 corresponds to C(7)).

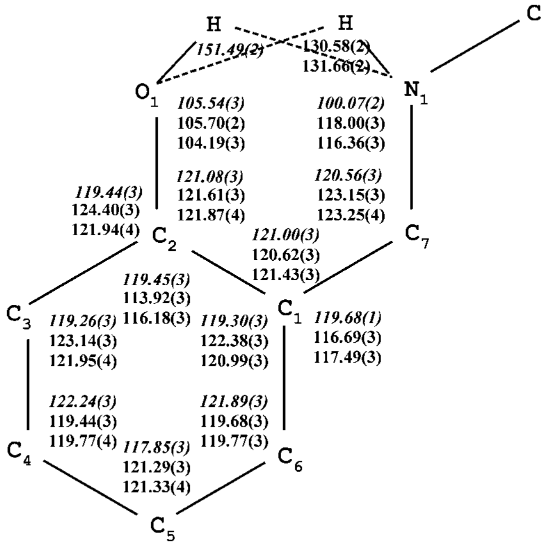


Figure 3. Valence angles [°] in **1** (in italics), **2** (second line) and **3** (third line).

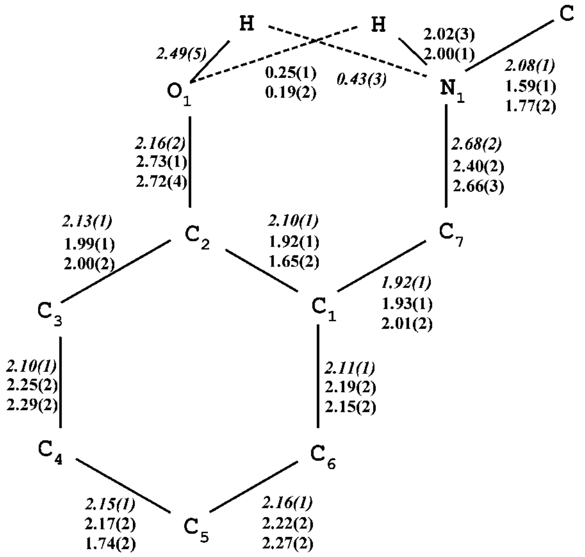


Figure 4. ρ at bond CPs [e Å^{-3}] in **1** (in italics), **2** (second line) and **3** (third line).

2.10(1) e Å^{-3}, respectively, whereas for the N–H forms these values are slightly smaller: 1.99(1) and 1.92(1) e Å^{-3} for **2** and 2.00(2) and 1.65(2) e Å^{-3} for **3**, with a consequent reduction of valence shell electron pair repulsion (VSEPR).[49] The covalent bonds to the hydrogen atoms participating in the hydrogen bonds have relatively large ρ_b values (2.49(5) e Å^{-3} for the O–H bond and 2.02(3) and 2.00(1) e Å^{-3} for the N–H bonds). This may be compared with an upper limit of 2.3 e Å^{-3} cited by Espinosa et al.[50] The value for the O–H bond is, in fact, higher than for the formally single C(2)–O(1) bond (2.16(2) e Å^{-3}). In the case of the N–H forms, the C(2)–O(1) bonds have more double-bond character with ρ_b approximately 2.7 e Å^{-3}. The ρ_b values for the aromatic C–C bonds seem to be quite typical (in the range 1.74–2.29 e Å^{-3}). The noncovalent hydrogen bonds have relatively small ρ_b equal to 0.43(3), 0.25(1) and 0.19(2) e Å^{-3} for **1**, **2** and **3**, respectively.

The distribution of laplacian for all three Schiff bases is shown in Figure 5. In the case of the **1** Schiff base, one observes a significant polarisation of the nitrogen lone pair towards the donor hydrogen atom. Comparing **2** and **3**, formation of the dimer by the latter (see next section) seems to be reflected in the shape of the laplacian distribution around the donor hydrogen atom, which is polarised towards both acceptor oxygen atoms in **3**.

In general, the values of the laplacian ($\nabla^2\rho_b$) at BCPs reflect the trends of the ρ_b values discussed above (see Figure 6). For example, the O–H and N–H bonds have large negative values of laplacian, namely, −27.4(3), −30.3(2) and −22.4(2) e Å^{-5} for **1**, **2** and **3**, respectively, compared with the value of −21.2(1) e Å^{-5} for C(2)–O(1) in **1**. We also want to point out that the hydrogen···acceptor CPs are in regions of positive

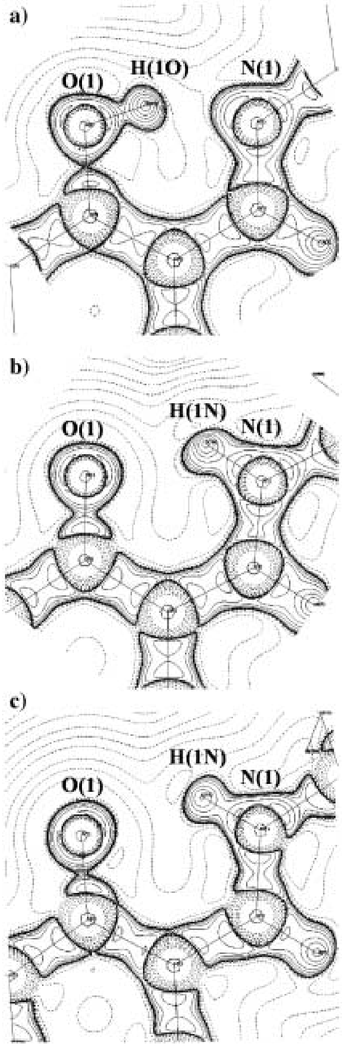


Figure 5. Laplacian maps in the plane of the hydrogen bond rings: a) **1**, b) **2** and c) **3** computed from the experimental multipole populations. Contours are at logarithmic intervals in $-\nabla^2\rho$ e Å^{-5}.

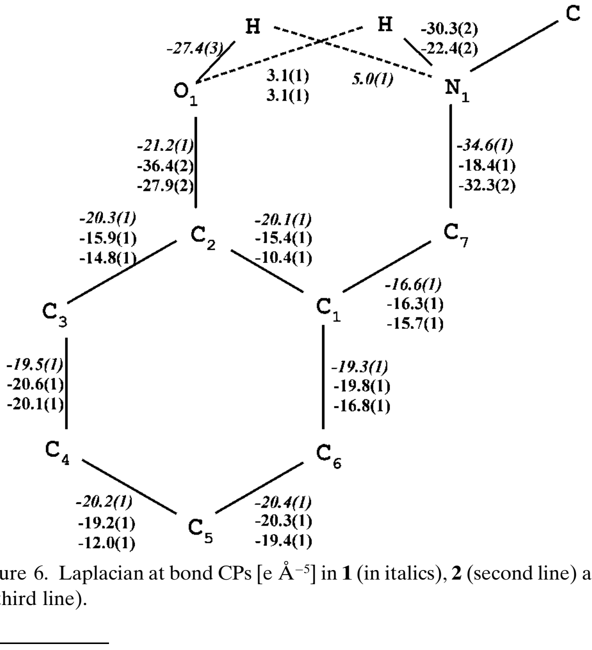


Figure 6. Laplacian at bond CPs [e Å^{-5}] in **1** (in italics), **2** (second line) and **3** (third line).

$\nabla^2\rho$, as is the case of the dichloromaleate anion in its complex with DMAN.[51]

It is possible to relate the charge density parameters at the H···acceptor critical points to local energy densities according to Equations (1) and (2):[52, 53]

$$G(r_{\mathrm{CP}}) = \frac{3}{10}(3\pi^2)^{2/3}\rho^{5/3}(r_{\mathrm{CP}}) + \frac{1}{6}\nabla^2\rho(r_{\mathrm{CP}}) \tag{1}$$

$$V(r_{\mathrm{CP}}) = \nabla^2\rho(r_{\mathrm{CP}}) - 2\,G(r_{\mathrm{CP}}) \tag{2}$$

in which $G(r_{\mathrm{CP}})$ is the local electronic kinetic energy density, ρ and ∇^2 are the electron density and laplacian at the CP, respectively, and V stands for the local potential-energy density. All quantities are in atomic units. According to such calculations, the values of $G(r_{\mathrm{CP}})$, with energy converted to SI units, for the intramolecular hydrogen bond in **1**, **2** and **3** are 166.2, 87.4, and 75.7 kJ mol^{-1} per atomic unit volume, respectively. The corresponding values of $V(r_{\mathrm{CP}})$ are -196.2, -91.2 and -66.6 kJ mol^{-1} per atomic unit volume. Espinosa et al.[53] have proposed a proportionality between the hydrogen-bond energy and the potential-energy density. Therefore, it appears that the hydrogen bond in **1** is approximately twice as strong as in **2** and three times as strong as in **3**.

Ellipticities at BCPs are defined in terms of the ratio of the curvatures of ρ_{b} in directions normal to the bond and represent the deviations of the bonding density from cylindrical symmetry. Their values are given in the Supporting Information, but the following ones are noteworthy. In the case of **1**, nearly all the values of ellipticities for aromatic BCPs are smaller than the values obtained for **2** and **3**, which means that formation of the O–H···N hydrogen bond reduces the double-bond character of the aromatic C–C bonds. Hence the aromaticity of the ring appears to be related to the position of the hydrogen-bonding hydrogen atom.

For the imine C(7)–N(1) bond the ellipticities are close to 0.17 for **1**, 0.11 for **2** and 0.43 for **3**; this means that in the first two compounds this bond is almost single, whereas in the third one it has a substantial double-bond character. A similar situation is found for the C(2)–O(1) bond. For the O···H and N···H hydrogen bonds, since the CP are in the region of positive laplacian, the ellipticity values have no significance.

The topology of the charge distribution in a molecule can be represented as a map of the bond paths and interaction lines connecting atomic nuclear positions, called a molecular graph. Figure 7 shows these graphs for all three molecules. A feature is a marked curvature of the hydrogen-bonding interaction lines for **2** and **3**. A similar phenomenon was found for some of the hydrogen bonds in dipicrylamine.[54]

Intermolecular interactions (dimers in 3): The crystal structure of **3** indicates the existence of both intra- and intermolecular hydrogen-bonded dimers, consisting of a pair of centrosymmetrically-related molecules. The interaction lines for this dimer are given in Figure 8.

The intermolecular hydrogen bond joins H(1N) to O(1) of a centrosymmetrically related molecule at a distance of 2.1456(3) Å, with the N(1)···O(1) donor–acceptor distance equal to 2.9398(5) Å. The corresponding hydrogen-bonding

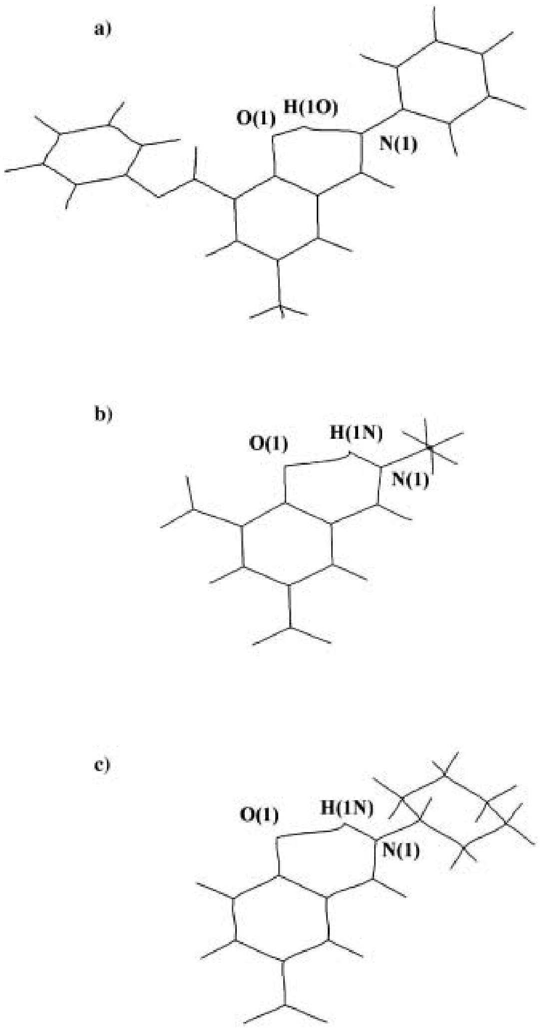


Figure 7. Bond paths and hydrogen-bond interaction lines for **1**, **2** and **3**.

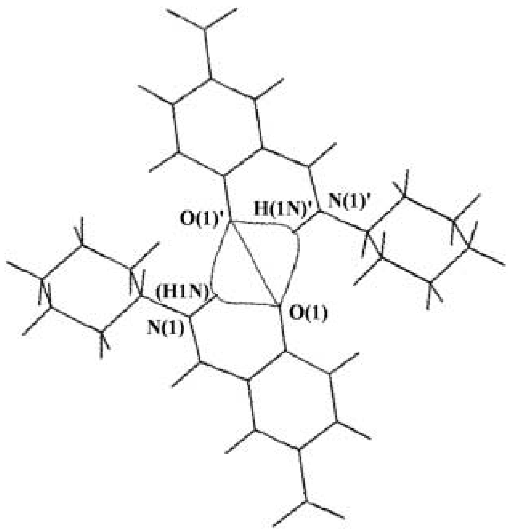


Figure 8. Interaction lines characterising inter- and intramolecular hydrogen bonding in **3**. Primed labels indicate symmetry code $-x, -y, -z$.

angle is 131.66(2)°. It also appears that there is an interaction line between symmetry related O(1) atoms with a CP at the centre of symmetry.

Conclusion

Properties of the hydrogen-bonded rings in the three Schiff bases studied show a variation depending on the position of the hydrogen atom. In the case of compound **1**, it is covalently bonded to the oxygen atom, and the hydrogen bond is neutral. Here the donor$\cdots$acceptor and H$\cdots$acceptor distances are shorter than for the compounds **2** and **3**, in which the hydrogen atom is covalently bonded to the nitrogen atom. This result is unexpected, since the two cases of ionic hydrogen bonds appear to have weaker interactions than that of a neutral hydrogen bond. However, it is supported by the analysis of local energy densities at the critical points and this situation is reflected, on average, in two series of compounds retrieved from the CSD.

There are also differences between the geometry and charge density parameters of the aromatic rings, corresponding to the neutral and ionic hydrogen-bond cases, consistent with the neutral hydrogen bond being stronger than the ionic ones with a consequent reduction in the aromaticity of the ring.

Compounds **2** and **3** both show a larger double-bond character in the C–O bond than appears in compound **1**, suggesting that the electronic structure of the former pair of compounds corresponds to a mixture of canonical forms **B** and **C**.

In the crystal structure of **3**, in addition to the intramolecular hydrogen bond, a pair of intermolecular O$\cdots$H interactions in a centrosymmetric dimer unit exist.

Experimental Section

Crystals of the Schiff bases studied were red (**1**) and yellow (**2** and **3**) prisms, grown by slow evaporation from acetonitrile. They were obtained by using the routine synthetic method of condensation of aldehydes with proper amines.[55] Single-crystal, high-resolution, low-temperature X-ray diffraction data for **1** and **2** were collected on the Brucker-Nonius kappa CCD diffractometer with an Oxford Cryosystems low-temperature attachment. For **3**, the CLRC Daresbury synchrotron radiation source (SRS) and Brucker SMART diffractometer at Station 9.8 was used. Data reduction and empirical absorption corrections were carried out with the DENZO and SORTAV[56] programs (**1** and **2**), whereas the data set for **3** was processed with the programs SAINT and SADABS.[57] Crystal data and other experimental details are given in Table 1.

Multipole refinement: The program XDLSM of the package XD[58] was used for the multipole refinement. Anisotropic temperature factors were applied to describe the thermal motion of non-hydrogen atoms. Scattering factors for C, H, O and N were derived from wavefunctions tabulated by Clementi and Roetti.[59] The multipole expansion was truncated at the octapole level for carbon, oxygen and nitrogen atoms, and at the dipole level for hydrogen atoms. Since all atoms are in general positions, the space group symmetry places no restrictions on the allowed multipole functions. Separate κ', and κ'' were employed for aromatic C, methylene C, N, O and H. Their values were allowed to vary, except those relating to H, which were fixed at 1.2.

CCDC-196735–196737 contain the supplementary crystallographic data for this paper. This data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

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