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The zwitterionic structure of 2-hydroxy-4-[(2-hydroxybenzylidene)amino]benzoic acid

Anderson A. B. C. Júnior, Gustavo S. G. De Carvalho, Lippy F. Marques, Charlane C. Corrêa, Adilson D. Da Silva and Flávia C. Machado*

Department of Chemistry, Federal University of Juiz de Fora, Juiz de Fora, Minas Gerais 36036-900, Brazil
Correspondence e-mail: flavia.machado@ufjf.edu.br

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The title compound, $C_{14}H_{11}NO_4$, exists in the solid phase in the zwitterionic form, 2-{[(4-carboxy-3-hydroxyphenyl)iminium-yl]methyl}phenolate, with the H atom from the phenol group on the 2-hydroxybenzylidene ring transferred to the imine N atom, resulting in a strong intramolecular N—H···O hydrogen bond between the iminium H atom and the phenolate O atom, forming a six-membered hydrogen-bonded ring. In addition, there is an intramolecular O—H···O hydrogen bond between the carboxylic acid group and the adjacent hydroxy group of the other ring, and an intermolecular C—H···O contact involving the phenol group and the C—H group adjacent to the imine bond, connecting the molecules into a two-dimensional network in the $(10\overline{3})$ plane. π–π stacking interactions result in a three-dimensional network. This study is important because it provides crystallographic evidence, supported by IR data, for the iminium zwitterionic form of Schiff bases.

Keywords: crystal structure; carboxylic acids; zwitterionic structures; Schiff bases.

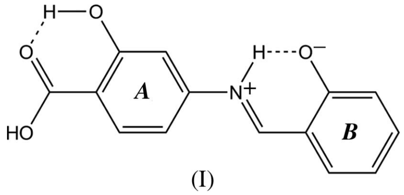
1. Introduction

Schiff bases, characterized by the –N=CH– (imine) group, constitute an important class of organic compounds. They are used as intermediates in organic synthesis or as ligands in coordination chemistry. The name Schiff bases refers to Hugo Schiff, whose studies involving aniline generated important information about the chemistry of imine compounds (Tidwell, 2008). They are used in optical and electrochemical sensors, and in biological systems like antibiotics and anti-allergic, antiphlogistic and antitumour substances (Layer, 1963). Schiff bases derived from the salicylaldehyde family exhibit a strong binding ability because of the presence of N/O donors, and they act as ligands in inorganic chemistry (Yao *et al.*, 2006; Le Guennic *et al.*, 2007).

2. Experimental

2.1. Synthesis and crystallization

In a 100 ml flask, 4-aminosalicylic acid (10.0 mmol, 1.0 g) was dissolved in methanol (20 ml) and salicylaldehyde (11.0 mmol, 1.1 g) was added. The mixture was stirred at room temperature for 1 h. After this time, an orange precipitate was isolated by filtration. The solid was dissolved in hot tetrahydrofuran (T = 333 K) and the resulting solution was set aside. After 4 d, orange crystals of (I) suitable for single-crystal X-ray diffraction analysis were collected (yield 73%; m.p. 432 K). Elemental analysis calculated for $C_{14}H_{11}NO_4$: C 65.37, H 4.31, N 5.44%; found: C 64.54, H 4.49, N 5.32%. IR spectroscopic data were obtained with a Bruker FT–IR spectrometer using KBr disks and a resolution of 4 cm^{-1}. The main absorption bands are (cm^{-1}): 3426 (νOH), 3049 (νC—H$_{\rm arom}$), 1642 (νC=O), 1608 (νC=N), 1512 (νC=C), and 791 and 762 ($\delta_{\rm oop}$C—H$_{\rm ar}$; oop = out of plane).



(I)

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. O- and N-bound H atoms were initially located in a difference Fourier map and were then added in idealized positions and further refined according to the riding model, with O—H = 0.82 Å and N—H = 0.86 Å, and with $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(O) or 1.2$U_{\rm eq}$(N). C-bound H atoms were included in the riding-model approximation, with C—H = 0.95 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C).

3. Results and discussion

The title Schiff base, (I) (Fig. 1), crystallizes in the monoclinic space group $P2_1/n$ with four molecules in the unit cell. Selected bond lengths and angles are presented in Table 2. The compound crystallizes in the zwitterionic form, with an anionic phenolate and a cationic iminium group.

The C8—N1 bond length [1.3067 (17) Å] agrees well with the double-bond character of imine groups in other zwitterion

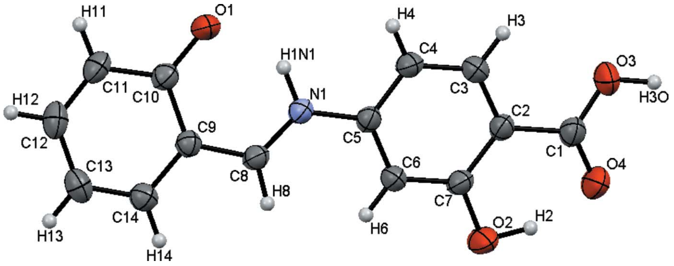


Figure 1
A view of asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

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Table 1
Experimental details.

Crystal data	
Chemical formula	$C_{14}H_{11}NO_4$
M_r	257.24
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	298
a, b, c (Å)	3.8393 (1), 18.3309 (4), 16.4738 (4)
β (°)	96.212 (2)
V (Å^3)	1152.58 (5)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.11
Crystal size (mm)	0.62 × 0.34 × 0.12
Data collection	
Diffractometer	Agilent Xcalibur diffractometer with an Atlas Gemini Ultra detector
Absorption correction	Analytical [*CrysAlis PRO* (Agilent, 2012), based on expressions derived by Clark & Reid (1995)]
T_{min}, T_{max}	0.973, 0.994
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	57654, 2349, 2006
R_{int}	0.038
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.625
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.037, 0.112, 1.03
No. of reflections	2349
No. of parameters	173
No. of restraints	0
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.20, −0.20

Computer programs: *CrysAlis PRO* (Agilent, 2012), *SHELXS97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 2008), *ORTEP-3 for Windows* (Farrugia, 2012), *Mercury* (Macrae *et al.*, 2008), *publCIF* (Westrip, 2010) and *WinGX* (Farrugia, 2012).

Schiff bases described in the literature, *e.g.* 1.306 (19) and 1.310 (2) Å (Makal *et al.*, 2011; Eltayeb, Teoh, Chantrapromma & Fun, 2010). The *trans* configuration relative to the C8—N1 bond can be inferred from the C9—C8—N1—C5 torsion angle of −176.72 (12)°. Aromatic rings *A* (C2–C7) and *B* (C9–C14) are not coplanar and are twisted with a dihedral angle of 19.34 (7)°. The iminium H atom is close to the phenolate O atom, allowing the formation of an intramolecular hydrogen bond (N1—H1N···O1; Table 3), in which the donor–acceptor distance is 2.5682 (15) Å, indicating a strong hydrogen bond with a highly covalent character (Makal *et al.*, 2011). This kind of interaction has been observed in other phenolate–imine zwitterions in which these groups are close to each other, for example, in (*E*)-4-hydroxy-2-{[(2-phenylethyl)iminiumyl]methyl}phenolate and 4-nitro-1-oxo-2-{(*E*)-[2-(piperidin-1-yl)ethyl]iminiomethyl}cyclohexadienide, with N···O = 2.5884 (15) and 2.674 (3) Å, respectively (Ortegon-Reyna *et al.*, 2012; Santos-Contreras *et al.*, 2009). Another strong intramolecular interaction [O2—H2···O4 = 2.5669 (17) Å], with the same behaviour, is observed between the carbonyl O atom of the carboxylic acid group and the phenol H atom of ring *A*. In both cases, six-membered rings are formed and, according to Etter's rule (Etter, 1990), this kind of intramolecular hydrogen bond is formed in preference to an intermolecular hydrogen bond. The reasoning behind this rule is based on the same kind of idea as the chelate effect in inorganic chemistry and is entropically favoured.

Atom O1 forms a strong intermolecular hydrogen bond with the hydroxy H atom of the carboxylic acid group of an adjacent molecule [O3—H3O···O1^i = 2.5058 (15) Å; symmetry code: (i) $x - \frac{3}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$]. This interaction links the molecules into one-dimensional zigzag chains running in the [301] direction (Fig. 2). The same behaviour has been observed in similar compounds, for example, (*E*)-4-bromo-2-[(2-hydroxyphenyl)iminiomethyl]phenolate (Eltayeb, Teoh, Fun & Chantrapromma, 2010). The zigzag chains interact with each other through weak intermolecular hydrogen bonds between the phenol O atom and the imine C—H group [C8—

Table 2
Selected geometric parameters (Å, °).

O1—C10	1.3008 (17)	N1—C8	1.3067 (17)
O3—C1	1.2975 (18)	N1—C5	1.4095 (16)
O2—C7	1.3497 (16)	O4—C1	1.2319 (17)
C8—N1—C5	127.39 (11)	N1—C8—C9	122.95 (12)
C8—N1—C5—C4	−167.01 (13)	C3—C4—C5—N1	−176.00 (13)
C8—N1—C5—C6	15.2 (2)	N1—C5—C6—C7	176.29 (13)
C5—N1—C8—C9	−176.72 (12)	C5—C6—C7—O2	−179.38 (13)
O3—C1—C2—C3	1.6 (2)	N1—C8—C9—C10	2.52 (19)
O3—C1—C2—C7	−178.75 (13)	N1—C8—C9—C14	−176.53 (12)
O4—C1—C2—C3	−178.39 (15)	C8—C9—C10—O1	1.19 (18)
O4—C1—C2—C7	1.3 (2)	C14—C9—C10—O1	−179.78 (12)
C1—C2—C7—O2	0.8 (2)	O1—C10—C11—C12	−179.66 (13)
C3—C2—C7—O2	−179.45 (13)		

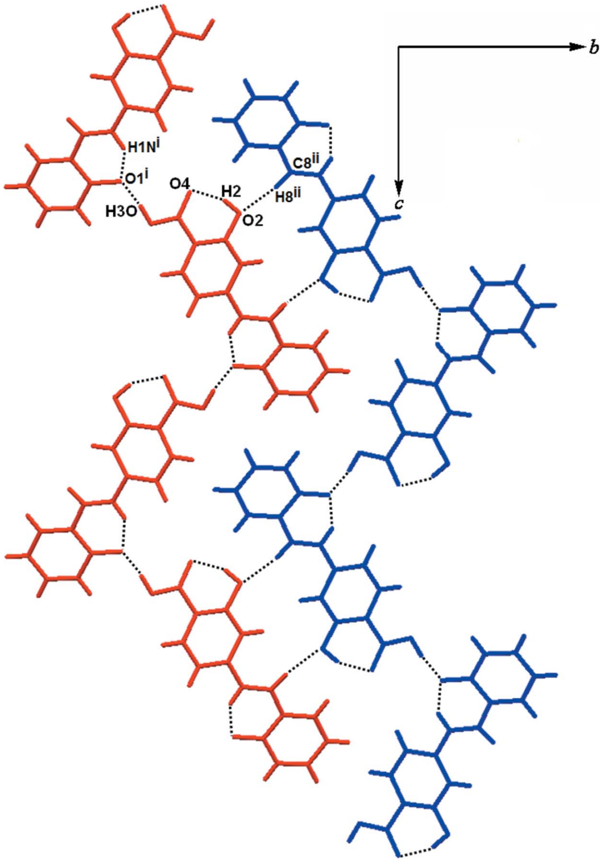

Figure 2
The bidimensional molecular network in (I) generated by O—H···O and C—H···O hydrogen bonds (dashed lines). [Symmetry codes: (i) $x - \frac{3}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (ii) $-x, -y + 1, -z$.]

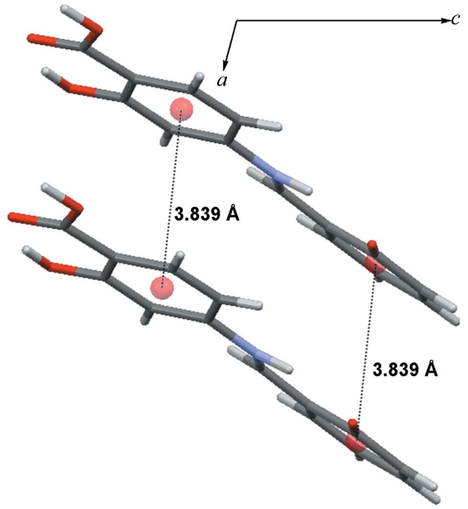

Figure 3
An illustration of the π–π stacking interactions in (I). Spheres denote the ring centroids.

H8$\cdots$O2^{ii}; symmetry code: (ii) $-x, -y+1, -z$], forming a two-dimensional network parallel to the $(10\overline{3})$ plane (Fig. 2). Using graph-set notation (Etter, 1990), the hydrogen-bonding system can be described as N1 = $C(12)S(6)R_2^2(14)$ and N2 = $R_6^6(46)$. These two intramolecular interactions and the above-mentioned intermolecular O3—H3O$\cdots$O1^{i} interaction have the same dimensions and behaviour as those in 2-[(*E*)-(3-carboxy-4-hydroxyphenyl)iminiomethyl]-4-chlorophenolate (Farag *et al.*, 2010). The only difference between these two structures is the presence of one chlorine substituent in the compound described in the literature. Although an additional intermolecular interaction is formed with the Cl atom, the dimensionality of the network is the same. A three-dimensional network arises in (I) through π–π stacking interactions between parallel aromatic rings from different two-dimensional layers (Fig. 3). Geometric details for this interaction are (Spek, 2009), for $A\cdots A(x-1, y, z)$, centroid–centroid distance = 3.8393 (8) Å, perpendicular distance = 3.4862 (6) Å and ring slippage = 1.608 (1) Å, and for $B\cdots B(x-1, y, z)$, centroid–centroid distance = 3.8393 (8) Å, perpendicular distance = 3.3671 (6) Å and ring slippage = 1.845 (1) Å.

Table 3
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1N$\cdots$O1	0.86	1.88	2.5682 (15)	136
O2—H2$\cdots$O4	0.82	1.84	2.5669 (17)	147
O3—H3O$\cdots$O1^{i}	0.82	1.70	2.5058 (15)	167
C3—H3$\cdots$O3	0.93	2.44	2.7502 (18)	100
C8—H8$\cdots$O2^{ii}	0.93	2.50	3.3725 (17)	156

Symmetry codes: (i) $x-\frac{3}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$; (ii) $-x, -y+1, -z$.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3499). Services for accessing these data are described at the back of the journal.

References

Agilent (2012). *CrysAlis PRO*. Agilent Technologies UK Ltd, Yarnton, Oxfordshire, England.
Clark, R. C. & Reid, J. S. (1995). *Acta Cryst.* A**51**, 887–897.
Eltayeb, N. E., Teoh, S. G., Chantrapromma, S. & Fun, H.-K. (2010). *Acta Cryst.* E**66**, o934–o935.
Eltayeb, N. E., Teoh, S. G., Fun, H.-K. & Chantrapromma, S. (2010). *Acta Cryst.* E**66**, o1262–o1263.
Etter, M. C. (1990). *Acc. Chem. Res.* **23**, 120–126.
Farag, A. M., Guan, T. S., Osman, H., Hemamalini, M. & Fun, H.-K. (2010). *Acta Cryst.* E**66**, o2466.
Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
Layer, R. W. (1963). *Chem. Rev.* **63**, 489–510.
Le Guennic, B., Petit, S., Chastanet, G., Pilet, G., Amor, N. B. & Robert, V. (2007). *Inorg. Chem.* **47**, 572–577.
Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
Makal, A., Schilf, W., Kamienski, B., Szady-Chelmieniecka, A., Grech, E. & Wozniak, K. (2011). *Dalton Trans.* **40**, 421–430.
Ortegon-Reyna, D., Garcias-Morales, C., García-Báez, E. V., Ariza-Castolo, A. & Martínez-Martínez, F. J. (2012). *Acta Cryst.* E**68**, o2075.
Santos-Contreras, R. J., Ramos-Organillo, A., García-Báez, E. V., Padilla-Martínez, I. I. & Martínez-Martínez, F. J. (2009). *Acta Cryst.* C**65**, o8–o10.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Tidwell, T. T. (2008). *Angew. Chem. Int. Ed.* **47**, 1016–1020.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
Yao, S.-Q., Zhu, M.-L., Lu, L.-P. & Gao, X.-L. (2006). *Acta Cryst.* C**62**, m183–m185.