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2-[(2-Hydroxy-4-nitrophenyl)aminomethylene]cyclohexa-3,5-dien-1(2*H*)-one

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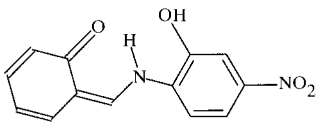
The title compound, $C_{13}H_{10}N_2O_4$, adopts the keto–amine tautomeric form and displays an intramolecular N—H···O [N···O = 2.579 (2) Å] and three intermolecular O—H···O [O···O = 2.561 (2) Å] and C—H···O [C···O = 3.274 (2) and 3.318 (2) Å] hydrogen bonds. The keto–amine structure is favoured by through-molecule conjugation between the hydroxy O atom and imine N atom. The dihedral angle between the planes of the two aromatic rings is 10.79 (4)°.

Comment

The extensive application of Schiff bases in industry and in analytical determinations has attracted attention for decades. *N*-Substituted *ortho*-hydroxyimines have been reported to display thermochromism and photochromism in the solid state by H-atom transfer from the hydroxy O atom to the N atom (Hadjoudis *et al.*, 1987; Xu *et al.*, 1994). The overall behaviour of these compounds has been ascribed to a proton-transfer reaction between a phenol–imine and a keto–amine tautomer. In solution, the existence of this tautomerism, which depends on the formation of intramolecular hydrogen bonds, is possible (Filarowski & Koll, 1998; Yıldız *et al.*, 1998; Nazır *et al.*, 2000; Deziembowska *et al.*, 2001; Ünver *et al.*, 2001). It is claimed that phenol–imine tautomerism is dominant in salicylaldimine, while the keto–amine form is preferred in naphthaldimine Schiff bases, depending on the solvent polarities. However, in the solid state, it is specified that keto–amine tautomerism is present in naphthaldimine, while the phenol–imine form exists in salicylaldimine Schiff bases (Kaitner & Pavlovic, 1996; Yıldız *et al.*, 1998). Our X-ray investigation of the title compound, (I), has indicated that the keto–amine tautomer is favoured over the phenol–imine tautomer.



(I)

An *ORTEP*-3 (Farrugia, 1997) view of the molecule of (I) and a packing diagram are shown in Figs. 1 and 2, respectively. The crystal and molecular structure of (I) reveals some interesting features. There is a strong intramolecular N—H···O hydrogen bond, with the H atom transferred from the O to the N atom; this intramolecular hydrogen bond is shorter than the sum of the van der Waals radii of oxygen and nitrogen (3.07 Å; Bondi, 1964). There is also an intermolecular O—H···O hydrogen bond, characterized by a relatively short O1···O2 distance [shorter than the sum of the van der Waals radii of two O atoms (3.04 Å; Pizzala *et al.*, 2000)]. The strong O···O hydrogen bond facilitates the H-atom transfer from the O to the N atom. Each molecule of (I) also participates in weak C3—H3···O3 and C2—H2···O4 hydrogen bonds, details of which are given in Table 2.

The salicylidene ring in (I) is significantly deformed from a regular hexagonal geometry, and this deformation can be explained by a possible through-resonance effect between the electron-donating O atom and the two-electron-accepting imino N atom. This effect also causes the elongation of the C1—C2 and C1—C6 bonds, and of both the carbonyl group and the exocyclic double bond on the salicylidene ring. The C1=O1 and N1—C7 bond lengths are 1.298 (2) and 1.308 (2) Å, respectively (Table 1), and these values correspond to those expected for a keto–amine structure (Hökelek

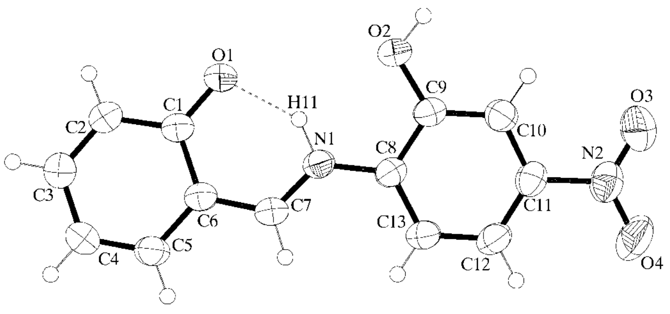


Figure 1
A view of the molecule of (I), showing the atom-labelling scheme and displacement ellipsoids at the 50% probability level.

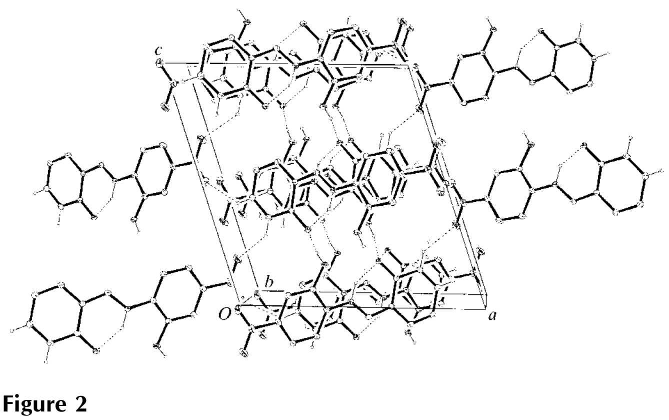


Figure 2
A packing diagram of (I), showing the hydrogen-bonding scheme.

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et al., 2000; Pizzala *et al.*, 2000). The C1═O1 bond length is consistent with other C═O double bonds [the C═O bond lengths are in the range 1.289–1.304 Å in 3-hydroxysalicylaldehyde derivatives (Pizzala *et al.*, 2000), 1.274 Å in 1-[*N*-(2-pyridyl)aminomethylidene]-2(1*H*)-naphthalenone (Hökelek *et al.*, 2000) and 1.263 Å in *N*-(2-pyridyl)-2-oxo-1-naphthylidenemethylamine (Nazır *et al.*, 2000)], and the N1—C7 distance is typical for an N—C single bond. Furthermore, the hypothesis that (I) exists in the keto–amine form is supported by the lengths of the C1—C2 and C1—C6 bonds. X-ray structure determination reveals that the keto–amine tautomer is favoured over the phenol–imine tautomer. A similar form is observed in 4-[(3-chlorophenyl)diazenyl]-2-{[tris(hydroxymethyl)methyl]aminomethylene}cyclohexa-3,5-dien-1(2*H*)-one (Odabaşoğlu *et al.*, 2003).

Experimental

To a solution of salicylaldehyde (2.44 g, 20 mmol) in butan-1-ol (75 ml) was added a solution of 2-hydroxy-4-nitroaniline (3.08 g, 20 mmol) in butan-1-ol (75 ml). The mixture was stirred under reflux, and the water occurring in the reaction was distilled out of the reaction mixture. The resulting red precipitate was filtered off and well shaped crystals of (I) were obtained by slow evaporation from ethyl alcohol (yield 90%).

Crystal data

$C_{13}H_{10}N_2O_4$
$M_r = 258.23$
Monoclinic, $P2_1/c$
$a = 11.9528\ (13)$ Å
$b = 8.0910\ (5)$ Å
$c = 12.4205\ (14)$ Å
$\beta = 108.268\ (9)°$
$V = 1140.65\ (19)$ Å^3
$Z = 4$
$D_x = 1.504$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8569 reflections
$\theta = 3.3–24.2°$
$\mu = 0.11$ mm^{-1}
$T = 293\ (2)$ K
Prism, red
0.60 × 0.30 × 0.25 mm

Data collection

Stoe IPDS-II diffractometer
ω scans
8738 measured reflections
2494 independent reflections
1961 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.036$
$\theta_{\rm max} = 27.1°$
$h = -15 \rightarrow 13$
$k = -10 \rightarrow 9$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.108$
$S = 1.04$
2494 reflections
181 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0695P)^2 + 0.0297P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.15$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.15$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.056 (8)

All H-atom positions were calculated using a riding model [C—H = 0.93 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C)], except for the H atom involved in the N—H···O hydrogen bond and the hydroxy H atom, which were found in difference Fourier maps and refined.

Table 1
Selected geometric parameters (Å, °).

C1—O1	1.298 (2)	C11—N2	1.465 (2)
C7—N1	1.308 (2)	N2—O3	1.214 (2)
C8—N1	1.407 (2)	N2—O4	1.219 (2)
C9—O2	1.346 (2)		
O1—C1—C2	121.7 (2)	C10—C11—N2	118.1 (2)
O1—C1—C6	121.4 (2)	C12—C11—N2	119.0 (2)
N1—C7—C6	122.8 (2)	C7—N1—C8	128.1 (2)
C13—C8—N1	123.7 (2)	O3—N2—O4	123.0 (2)
C9—C8—N1	116.1 (2)	O3—N2—C11	118.1 (2)
O2—C9—C10	123.5 (2)	O4—N2—C11	118.8 (2)
O2—C9—C8	117.0 (2)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H11···O1	0.96 (2)	1.76 (2)	2.579 (2)	142.0 (15)
O2—H21···O1$^{\rm i}$	0.93 (2)	1.64 (2)	2.561 (2)	169.5 (2)
C3—H3···O3$^{\rm ii}$	0.93	2.52	3.274 (2)	138
C2—H2···O4$^{\rm iii}$	0.93	2.62	3.318 (2)	132

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

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED*32 (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1431). Services for accessing these data are described at the back of the journal.

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