

3-Hydroxy-6-[(4-hydroxyphenyl-amino)methylene]cyclohexa-2,4-dienone and 2-hydroxy-6-[(4-hydroxyphenylamino)-methylene]cyclohexa-2,4-dienone

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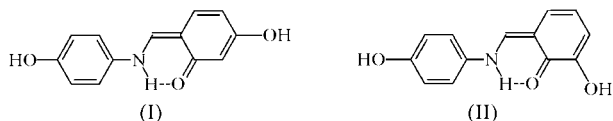
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The title compounds, both $C_{13}H_{11}NO_3$, exist as the keto–amine tautomers, and the formal hydroxyl H atoms, which display strong intramolecular hydrogen bonds, are located on the N atoms. This is a verification of the preference for the keto–amine tautomeric form in the solid state. The 2-hydroxy isomer has two independent molecules, with the molecules linked by intramolecular $N-H\cdots O$ and $O-H\cdots O$ and intermolecular $O-H\cdots O$ hydrogen bonds into three-dimensional networks.

Comment

o-Hydroxy Schiff bases, derived from the reaction of *o*-hydroxyaldehydes with aniline, have been extensively examined (Steward & Lingafelter, 1959; Calligaris *et al.*, 1972; Maslen & Waters, 1975). These Schiff base compounds display interesting photochromic and thermochromic features and can be classified by them (Cohen *et al.*, 1964; Moustakali-Mavridis *et al.*, 1980; Hadjoudis *et al.*, 1987). Photo- and thermochromism arise *via* H-atom transfer from the hydroxy O atom to the N atom (Hadjoudis *et al.*, 1987; Xu *et al.*, 1994).



There are two types of intramolecular hydrogen bonds in Schiff bases arising from the keto–amine ($N-H\cdots O$) and enol–imine ($N\cdots H-O$) tautomeric forms. The present X-ray investigation shows that the title compounds, (I) and (II), prefer keto–amine tautomerism rather than enol–imine tautomerism. *o*-Hydroxy Schiff bases have been previously observed in the keto form (Ünver, Kabak *et al.*, 2002; Odabaşoğlu, Albayrak, Büyükgüngör & Goesmann, 2003;

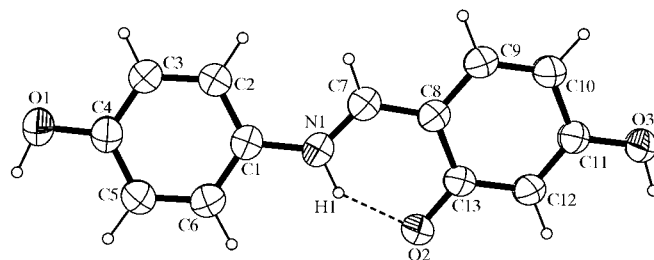


Figure 1

A view of (I), with the atom-numbering scheme and 50% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii.

Koşar *et al.*, 2004; Hökelek *et al.*, 2000), in the enol form (Karadayı *et al.*, 2003; Leardini *et al.*, 1998; Ünver, Yıldız *et al.*, 2002; Elmalı *et al.*, 1998) or in enol/keto mixtures (Nazır *et al.*, 2000), by means of H-atom transfer. Related to this phenomenon, we present here the structures of (I) and (II).

The molecular structure of (I) is shown in Fig. 1, with the atom-numbering scheme. Selected bond lengths and angles are listed in Table 1. The $C13-O2$ and $C7-N1$ bond lengths verify the keto–amine form of compound (I). These distances agree with the corresponding distances in 2-[[tris(hydroxymethyl)methyl]aminomethylene]cyclohexa-3,5-dien-1(2*H*)-one [1.3025 (16) and 1.2952 (18) Å; Odabaşoğlu, Albayrak, Büyükgüngör & Lönnecke, 2003] and 3-[(2-oxo-1-naphthylidene)methylamino]benzoic acid [1.290 (2) and 1.319 (3) Å; Pavlović & Sosa, 2000], which also show the keto–amine tautomeric form. The same bonds can be compared with the corresponding distances in *N*-(2-fluoro-3-methoxy)salicylaldehyde [1.347 (3) and 1.280 (3) Å; Ünver, Kendi *et al.*, 2002] and *N*-[3,5-bis(trifluoromethyl)phenyl]-3-methoxysalicylaldehyde [1.352 (3) and 1.280 (4) Å; Karadayı *et al.*, 2003], which exist in the enol–imine tautomeric form.

Compound (I) displays a strong intramolecular $N-H\cdots O$ hydrogen bond between atoms N1 and O2 (Table 2). This type of strong intramolecular hydrogen bond is a common feature of *o*-hydroxysalicylidene systems (Filarowski *et al.*, 2003; Yıldız *et al.*, 1998; Odabaşoğlu, Albayrak, Büyükgüngör &

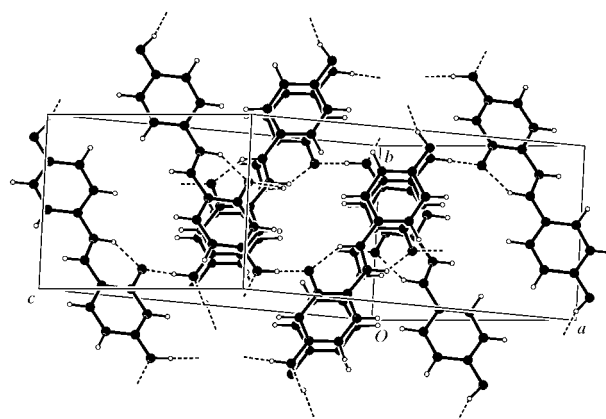


Figure 2

A packing diagram for (I). Dashed lines indicate intra- and intermolecular hydrogen bonds.

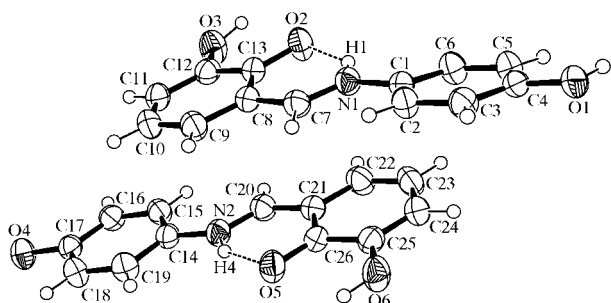


Figure 3
A view of (II), with the relative positions of the two independent molecules.

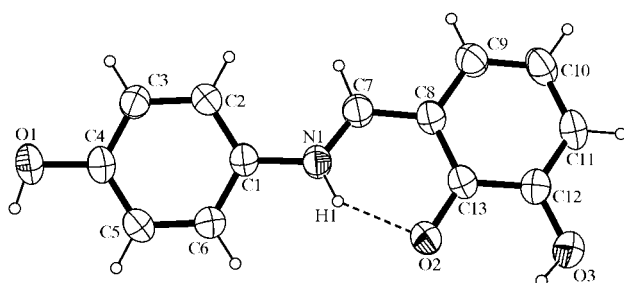


Figure 4
A view of one of the two independent molecules of (II), with the atom-numbering scheme and 50% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii.

Lönnecke, 2003). The N—H···O hydrogen-bonded ring is coplanar with the adjacent ring, with an N1—C7—C8—C13 torsion angle of 0.0 (3)°.

Compound (II) is very similar to (I), with two independent molecules. Fig. 3 shows the positions of these two independent molecules relative to each other. Because of the different positions of the hydroxyl groups in (I) and (II), there are differences in the bond lengths and angles between the two compounds. Fig. 4 shows the molecular structure of (II), with the atom-numbering scheme. Selected bond lengths and angles for (II) are listed in Table 3. Compound (II) has two strong intramolecular N—H···O hydrogen bonds and an intramolecular O—H···O hydrogen bond (Table 4). The N1—H1···O2 hydrogen-bonded ring of (II) is planar and forms a torsion angle with the adjacent ring of 0.2 (5)°. The N2—H4···O5 hydrogen-bonded ring is also planar and is coupled with the adjacent ring, with an N2—C20—C21—C26 torsion angle of 1.4 (5)°.

Experimental

The title compounds were prepared as described by Odabaşoğlu, Albayrak, Büyükgüngör & Goesmann (2003), using 4-hydroxyaniline and 4-hydroxysalicylaldehyde as starting materials for (I), and 4-hydroxyaniline and 3-hydroxysalicylaldehyde for (II). Well shaped crystals were obtained by slow evaporation from ethanol solutions [for (I): yield 82%, m.p. 504–506 K; for (II): yield 85%, m.p. 464–4660 K].

Compound (I)

Crystal data

$C_{13}H_{11}NO_3$
 $M_r = 229.23$
Monoclinic, $C2/c$
 $a = 13.2579$ (11) Å
 $b = 7.8772$ (8) Å
 $c = 20.4502$ (15) Å
 $\beta = 91.369$ (6)°
 $V = 2135.1$ (3) Å³
 $Z = 8$

$D_x = 1.426$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 6435 reflections
 $\theta = 2.0$ – 27.7 °
 $\mu = 0.10$ mm⁻¹
 $T = 293$ (2) K
Cylindrical, dark red
 $0.45 \times 0.35 \times 0.21$ mm

Data collection

Stoe IPDS-II diffractometer
 ω scans
Absorption correction: by integration (*X-RED*; Stoe & Cie, 2002)
 $T_{\min} = 0.965$, $T_{\max} = 0.982$
10 511 measured reflections
2486 independent reflections

1563 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.058$
 $\theta_{\max} = 27.7$ °
 $h = -17 \rightarrow 17$
 $k = -10 \rightarrow 10$
 $l = -24 \rightarrow 26$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.044$
 $wR(F^2) = 0.123$
 $S = 0.94$
2486 reflections
199 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0753P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.16$ e Å⁻³
 $\Delta\rho_{\min} = -0.16$ e Å⁻³
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.0077 (14)

Table 1

Selected geometric parameters (Å, °) for (I).

C1—N1	1.4174 (19)	C7—C8	1.398 (2)
C4—O1	1.3568 (18)	C11—O3	1.3342 (17)
C7—N1	1.305 (2)	C13—O2	1.3101 (17)
C7—C8—C9	119.60 (13)	O2—C13—C12	122.19 (12)
C7—C8—C13	121.79 (13)	O2—C13—C8	119.33 (12)
N1—C7—C8—C13	0.0 (3)		

Table 2

Hydrogen-bonding geometry (Å, °) for (I).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N1—H1···O2	0.967 (19)	1.77 (2)	2.5976 (16)	141.0 (17)
O1—H11···O3 ⁱ	1.01 (3)	1.68 (3)	2.6619 (16)	165 (2)
O3—H33···O2 ⁱⁱ	0.947 (17)	1.531 (17)	2.4775 (14)	178 (3)

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

Compound (II)

Crystal data

$C_{13}H_{11}NO_3$
 $M_r = 229.23$
Monoclinic, $P2_1/c$
 $a = 12.6440$ (8) Å
 $b = 8.3499$ (3) Å
 $c = 20.1529$ (12) Å
 $\beta = 96.693$ (5)°
 $V = 2113.2$ (2) Å³
 $Z = 8$

$D_x = 1.441$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 22 130 reflections
 $\theta = 1.6$ – 27.1 °
 $\mu = 0.10$ mm⁻¹
 $T = 293$ (2) K
Shapeless, dark red
 $0.50 \times 0.45 \times 0.21$ mm

Data collection

Stoe IPDS-II diffractometer	3305 reflections with $I > 2\sigma(I)$
ω scans	$R_{\text{int}} = 0.033$
Absorption correction: by integration (<i>X-RED</i> ; Stoe & Cie, 2002)	$\theta_{\text{max}} = 27.0^\circ$
$T_{\text{min}} = 0.950$, $T_{\text{max}} = 0.985$	$h = -16 \rightarrow 16$
32 250 measured reflections	$k = -10 \rightarrow 10$
4610 independent reflections	$l = -25 \rightarrow 25$

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.034$	
$wR(F^2) = 0.093$	$w = 1/[\sigma^2(F_o^2) + (0.0592P)^2]$
$S = 0.98$	where $P = (F_o^2 + 2F_c^2)/3$
4610 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
339 parameters	$\Delta\rho_{\text{max}} = 0.21 \text{ e } \text{\AA}^{-3}$
	$\Delta\rho_{\text{min}} = -0.15 \text{ e } \text{\AA}^{-3}$

Table 3

Selected geometric parameters (\AA , $^\circ$) for (II).

C1–N1	1.416 (4)	C7–C8	1.428 (4)
C4–O1	1.381 (3)	C12–O3	1.365 (4)
C7–N1	1.288 (4)	C13–O2	1.324 (4)
C9–C8–C7	119.5 (3)	O2–C13–C12	120.0 (3)
C13–C8–C7	120.4 (3)	O2–C13–C8	122.1 (3)
N1–C7–C8–C13	0.2 (5)	N2–C20–C21–C26	1.4 (5)

Table 4

Hydrogen-bonding geometry (\AA , $^\circ$) for (II).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N2–H4 \cdots O5	1.04 (5)	1.64 (5)	2.561 (3)	145 (4)
N1–H1 \cdots O2	0.88 (5)	1.84 (4)	2.578 (3)	141 (6)
O6–H66 \cdots O5	0.88 (5)	2.22 (5)	2.686 (3)	112 (4)
O1–H77 \cdots O6 ⁱ	0.90 (5)	1.85 (5)	2.733 (4)	167 (4)
O6–H66 \cdots O2 ⁱⁱ	0.88 (5)	2.07 (6)	2.846 (4)	146 (5)
O4–H44 \cdots O1 ⁱⁱⁱ	0.91 (5)	1.90 (5)	2.803 (4)	167 (5)
O3–H33 \cdots O5 ^{iv}	0.92 (5)	1.89 (6)	2.727 (4)	150 (5)

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

For (I), all H-atom parameters were freely refined. C–H distances are in the range 0.95 (2)–1.022 (18) \AA and $U_{\text{iso}}(\text{H})$ values are in the range 0.058 (5)–0.126 (9) \AA^2 . For (II), all H atoms, except for H1, H4, H7, H20, H33, H44, H66 and H77, were treated using a riding model, with C–H = 0.93 \AA and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{parent atom})$. The

remaining H atoms were refined isotropically; the calculated C–H bond lengths are in the range 0.98 (4)–0.99 (4) \AA .

For both compounds, data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1477). Services for accessing these data are described at the back of the journal.

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